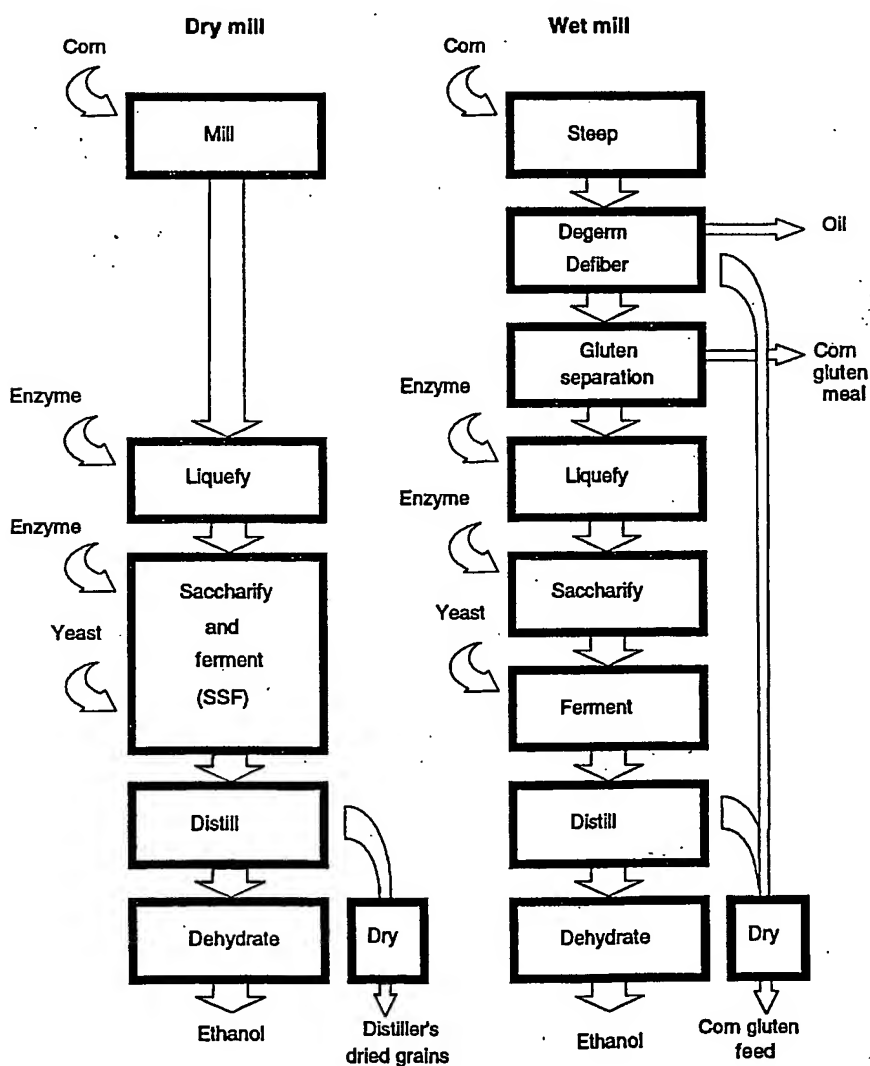


## REMARKS

Claims 1-3 have been cancelled without prejudice. Claims 4-5 had previously been withdrawn. New claims 6-8 are pending in this case.

The claimed invention is an improved ethanol production process. There are two basic ethanol production processes: wet milling and dry milling. The following flowchart (see Hohmann et al, USDA-ERS study entitled "*Emerging Technologies in Ethanol Production*" at p. 3) is illustrative of the basic steps in each of the two process.



Thus, in a dry milling ethanol production process ethanol is the primary product and a distiller's dried grain (DDG) or distiller's dried grain with solubles (DDGS) are principal the co-products obtained. Although not reflected in the above schematics some ethanol production plants also recover by distillation the carbon dioxide generated during the fermenting step. There have also been proposed modified ethanol product plants to recover lactic acid (e.g., U.S. Patent 5,503,750), zein proteins (e.g., U.S. Patent 7,045,607), and other valuable by-products contained in the corn feedstock or formed during the normal fermentation of the liquefied mash (e.g., U.S. Patent 5,316,782). In these prior art processes the approach has generally been to either to utilize a portion of the feedstock in a separate treatment process that may use some the ethanol produced as an extracting agent in the separate treatment process or that will use the by-product from the separate treatment process as a part of the feedstock to the ethanol production process. Other of these prior art processes propose modifying or specially treating the whole stillage or fractions thereof to obtain the desired by-product. In the traditional wet milling process ethanol is again the primary product. However, in this process the whole corn is first broken down into its various constituent parts. Each of the parts are then separately treated to obtain the desired by-products: corn oil from the germ, corn gluten meal and corn gluten feed from the hull, fibers and germ de-oiled residue. The starch-containing portion of the corn is then used to produce the ethanol.

However, in neither type of ethanol production process does any of these prior art processes teach or suggest modification by a secondary treatment agent the liquefied mash during the saccharification/fermentation step to produce a modified beer that contains the desired product, or precursor thereof.

It is important to understand the claimed invention differs from the prior art in that based on the feedstock it permits the plant operator previously unobtainable flexibility in selecting from a wide range of by-products what by-products can be recovered. Thus, if current market conditions change, and one possible by-product becomes more valuable than the currently produced by-products, the plant operator has the ability to modify the process by simply changing the secondary treatment agent with little or no effect on the amount of ethanol being recovered and without having to expend additional capital for equipment to generate the desired by-product. It has long been recognized (see p.8 of attached Hohman et al study) that one of the best potential economic gains in ethanol production process lies in the ability to obtain high-value by-products from the process. Despite this long felt need and the large sum of research monies and manpower spent no one prior to this invention has discovered a method that permits the flexibility of by-product selection without the need for expensive capital investment and without the loss of any significant ethanol production.

Applicants first recognized that the most desirable way to produce the desired by-product would be simultaneously with the saccharification or fermentation of the liquefied mash. This process step results in the desired by-product (or its precursor) being contained in the resulting beer. Thus, this step avoids the additional capital costs of separate process equipment found in many prior art processes that separately treat a portion of the feedstock to generate and recover desired by-products. In addition it permits the use of equipment already in place in a conventional ethanol production plant. Secondly, applicants discovered that this simultaneous step can be achieved without any significant decrease in ethanol production; i.e., applicants' process does not prevent the

formation of the beer. To persons of ordinary skill in ethanol production beer refers to the resultant fermentation product containing at least 10% v/v ethanol (see the attached USDA studies). If ethanol production is inhibited so that this beer can not be produced, then the economic viability of the ethanol production plant is questionable. Applicants claimed invention avoids both the need for expensive new equipment, as well as does not prevent the formation of the beer necessary for an economically viable ethanol production plant.

These unexpected benefits are achieved by the proper selection of the treatment agent that will be introduced directly into the fermentation vessel during the saccharification or fermentation step. The treatment agent must have the following characteristics:

- (a) the secondary treatment agent is selected from a group consisting of bacteria, enzymes, fungi, or combinations thereof, that can convert under the fermentation conditions at least a portion of the liquefied mash to a pre-selected non-ethanol by-product or precursors thereof;
- (b) the secondary treatment agent has the characteristics of remaining active in the presence of the ethanol contained in the beer being formed during the fermenting of the liquefied mash,
- (c) the secondary treatment agent under the fermentation conditions converts at least a portion of the liquefied mash during the fermenting of the liquefied mash into the pre-selected non-ethanol by-product or precursors thereof, and



(d) the activity of the secondary treatment agent does not prevent the fermentation of the liquefied mash to produce the beer having at least 10% ethanol by volume.

**Prior Art Cited in Previous Office Action**

In the June 7, 2007 Office Action it had been argued that the now cancelled claims 1-3 under 35 USC §102 (b) were anticipated by the Lima et al article entitled “*β-Cyclodextrin Production by Simultaneous Fermentation and Cyclization*.” Lima examines the production of *β-Cyclodextrin* from starch hydrolysates, such high-dextrose equivalent (DE) cassava starch based hydrolysates. More particularly, Lima discloses three primary methods for producing *β-Cyclodextrin* from a hydrolyzed cassava starch slurry. These three primary methods are: (i) treating the hydrolyzed cassava starch slurry only with CGTase enzyme, (ii) treating the hydrolyzed cassava starch slurry with both CGTase enzyme + ethanol, and (iii) treating the hydrolyzed cassava starch slurry with the combination of CGTase enzyme + yeast + nutrients. It is only in this latter method, referred to as the Simultaneous Fermentation and Cyclization Process (SFC Process), that both an enzyme and an yeast are used simultaneously to produce the desired *β-Cyclodextrin*.

There are significant differences between the Lima methods and the claimed ethanol production process defined in claims 6-8. First, none of the three primary methods disclosed in Lima are an ethanol production process. This is clearly pointed out by Lima in Table 2 at p. 802. Using the SFC Process results in the production of no more than 2.18% v/v ethanol even when DE=26.06. The other methods produce even less ethanol. Thus, none of the methods disclosed in Lima result in the production of

beer (i.e., containing >10% by volume ethanol) from the hydrolyzed cassava starch. Still further, there is no teaching or suggestion in Lima that both  *$\beta$ -Cyclodextrin* and beer could be produced simultaneously in a yeast fermentation process wherein CGTase is added to the fermentation vessel during the fermentation process. If anything, Lima would appear to teach that such results would not be expected.

Although not cited in the previous Office Actions applicants notes that there are prior art references that disclose the use of more than one saccharification agent or more than one fermenting agent. An example of such references is U.S. Patent 5,231,017 (copy attached). In these references the additional agent is selected for its ability to increase the amount of ethanol produced, and not for the formation of a pre-selected non-ethanol by-product that can be recovered in the resultant whole stillage.

### CONCLUSION

Based upon the foregoing comments, the application is believed to be in condition for allowance, and an early Notice of Allowability is respectfully requested. If the examiner believes a telephone conference will expedite the disposition of this matter, the examiner is respectfully invited to contact this attorney at the number shown below.

Respectfully submitted:

Dated: December 3, 2007

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Attachments:

- Hohmann et al, USDA-ERS study entitled “*Emerging Technologies in Ethanol Production*” (January 1993)
- Dien et al, USDA-ARS study entitled “*The U.S. Corn Ethanol Industry: An Overview of Current Technology and Future Prospects*” (April 2002)
- Rendleman et al, USDA Agricultural Economic Report No. 842 entitled “*New Technologies in Ethanol Production*” (February 2007)
- U.S. Department of Energy Office of Science article entitled “*Genomics:GTL – Systems Biology for Energy and Environment*” (original publication date not known)
- U.S. Patent 5,231,017
- U.S. Patent 5,316,782
- U.S. Patent 5,503,750
- U.S. Patent 7,045,607



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Agriculture

Economic  
Research  
Service

Agriculture  
Information  
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# Emerging Technologies in Ethanol Production

Neil Hohmann  
C. Matthew Rendleman



*The fuel ethanol industry is poised to adopt a wide range of technologies that would reduce costs at every stage of the production process. Improved enzymes and fermenter designs can reduce the time needed to convert corn to ethanol and lower capital costs. Membrane filtration can allow the recovery of high-value coproducts such as lactic acid. Adoption of these and other innovations in the next 5 years is expected in new ethanol plants constructed to cope with new demand resulting from Clean Air Act stipulations for cleaner burning fuel. Biomass (agricultural residues, municipal and yard waste, energy crops like switchgrass) can also be converted to ethanol, although commercial-scale ventures are limited by current technology. While biomass requires more handling and sorting before conversion, those costs may be offset by the abundance of biomass relative to corn.*

The use of ethanol as a fuel for vehicles in the United States grew from insignificance in 1977 to nearly 900 million gallons in 1991. The ethanol industry emerged through a combination of government incentives and new technologies, which enabled large-scale production of ethanol from domestic resources, particularly corn. Growing consumer acceptance of ethanol-blended fuels, incentives to gasoline blenders, and falling costs of production were responsible for the jump in ethanol production. This report examines the likelihood of obtaining further reductions in the cost of producing ethanol from the introduction of new technology.

Technological innovation in the ethanol production process has substantially reduced costs. A shift in production to larger plants and the adoption of energy-saving innovations reduced the processing energy required to produce a gallon of ethanol from 120,000 British thermal units (Btu) in 1981 to an industry average of 43,000 Btu in 1991, resulting in a positive net energy balance (Russo, 1991).<sup>1</sup> (See

endnotes at end of report.) The use of improved yeast strains has lowered processing costs. Improvements in enzymes have reduced their cost by more than 50 percent. Such innovations have collectively lowered total production costs from \$1.35-\$1.45 per gallon in 1980 to less than \$1.25 per gallon in 1992.

The construction of new ethanol production plants and the adoption of new technologies at existing plants is likely to lead to further cost reductions. We estimate that over the next 5 years the average cost of ethanol production in the industry will decline by 5-7 cents per gallon because of further technological innovations. Improved yeasts, which tolerate high concentrations of ethanol, can lower energy costs. A system of membranes can recycle enzymes and capture high-value coproducts at many steps in the production process.

Longer term technologies would save approximately 9-15 cents per gallon over present costs. Energy and feedstock savings will result from technology that can convert some of the nonstarch portions of corn to ethanol. Development of microorganisms that speed the process will contribute to long-term savings. Development of markets for coproducts of ethanol production will create additional savings. Cost savings may be less for smaller plants that serve niche markets, or in older plants that must replace inefficient equipment.

The cost of producing ethanol will also be greatly influenced by outside technological advances. Farm technologies that raise corn yields or reduce input costs may lower feedstock costs for ethanol production, as they have in the past. Refinements and new, higher value uses for coproducts are an even likelier source of new revenues and could reduce the cost of ethanol by as much as plant innovations.

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Finally, various forms of biomass--agricultural residues, woody or grassy energy crops, or even municipal waste--could supplement corn as an inexpensive feedstock for ethanol production. Although the production of ethanol from biomass is presently constrained by technological difficulties, new developments in this decade may allow ethanol to be produced from biomass at or below the cost of corn-derived ethanol.

## **The Conversion of Corn into Ethanol**

Ethanol is produced from corn by two standard processes: wet- and dry-milling (fig. 1).<sup>2</sup> Wet-milling accounts for about 60 percent of total ethanol production. Dry-milling plants cost less to build and produce higher yields of ethanol (2.6 gallons per bushel vs. 2.5 for wet mills), but the value of coproducts is less.

In each process, the corn is cleaned before it enters the mill. In a dry mill, the milling step consists of grinding the corn and adding water to form the mash. In a wet mill, milling and processing are more elaborate because the grain must be separated into its components. First, the corn is steeped in a solution of water and sulfur dioxide for 24-48 hours to loosen the germ and hull fiber. The germ is then removed from the kernel, and corn oil, a valuable coproduct, is extracted from the germ. The remaining germ meal is added to the hulls and fiber to form the corn gluten feed (CGF) stream. Gluten, a high-protein portion of the kernel, is also separated and becomes corn gluten meal (CGM), a high-value, high-protein (60 percent) animal feed.<sup>3</sup>

In wet-milling, only the starch is fermented, unlike dry-milling in which the entire mash is fermented. The starch is cooked, or liquefied, and an enzyme is added to hydrolyze (break into smaller chains) the starch. In dry-milling, the mash, still containing all the feed coproducts, is cooked, and an enzyme added. In both systems, a second enzyme is added to turn the starch into a simple sugar, glucose (a process called saccharification). Though it usually takes about 24 hours, saccharification in a wet mill may take up to 48 hours, depending on the amount of enzyme used. In modern dry mills, saccharification has been combined with the fermentation step in a process called simultaneous saccharification and fermentation (SSF).

The next step in both processes is the fermentation of glucose into ethanol by yeast (the SSF step in most dry mills). The mash must be cooled to at least 95° F before the yeast can be added. The yeast converts the glucose into ethanol, carbon dioxide, and small quantities of other organic compounds. The yeast, which produces almost as much carbon dioxide as ethanol, ceases fermenting when the concentration of alcohol is around 12 percent by volume.

Distillation, an energy-consuming process, is then required to separate the ethanol from the alcohol-water solution. This step consists of two parts, primary distillation and dehydration. Primary distillation yields ethanol that is up to 95 percent free of water. The dehydration step is necessary to bring the concentration of ethanol up to 99 percent. Several technological options are available for the dehydration step.<sup>4</sup> A small amount of gasoline is added to the ethanol to denature (make unfit for human consumption) it before it leaves the plant. The feed coproducts, CGF and CGM in wet-milling and distiller's dried grains and solubles (DDGS) in dry-milling, must be concentrated in large evaporators, then dried.

## **Costs of Production Under Present Technology**

The cost of producing ethanol depends on a number of factors including the cost of corn, the value of coproducts, the cost of energy and enzymes, the size of the production plant, and the level of technology in the plant. The development and adoption of new technology have been the center of a long-term industry strategy to increase the efficiency of inputs, speed up the production process, and raise the yield of ethanol. Costs of ethanol production are usually divided into three categories: feedstock, capital, and operating costs.

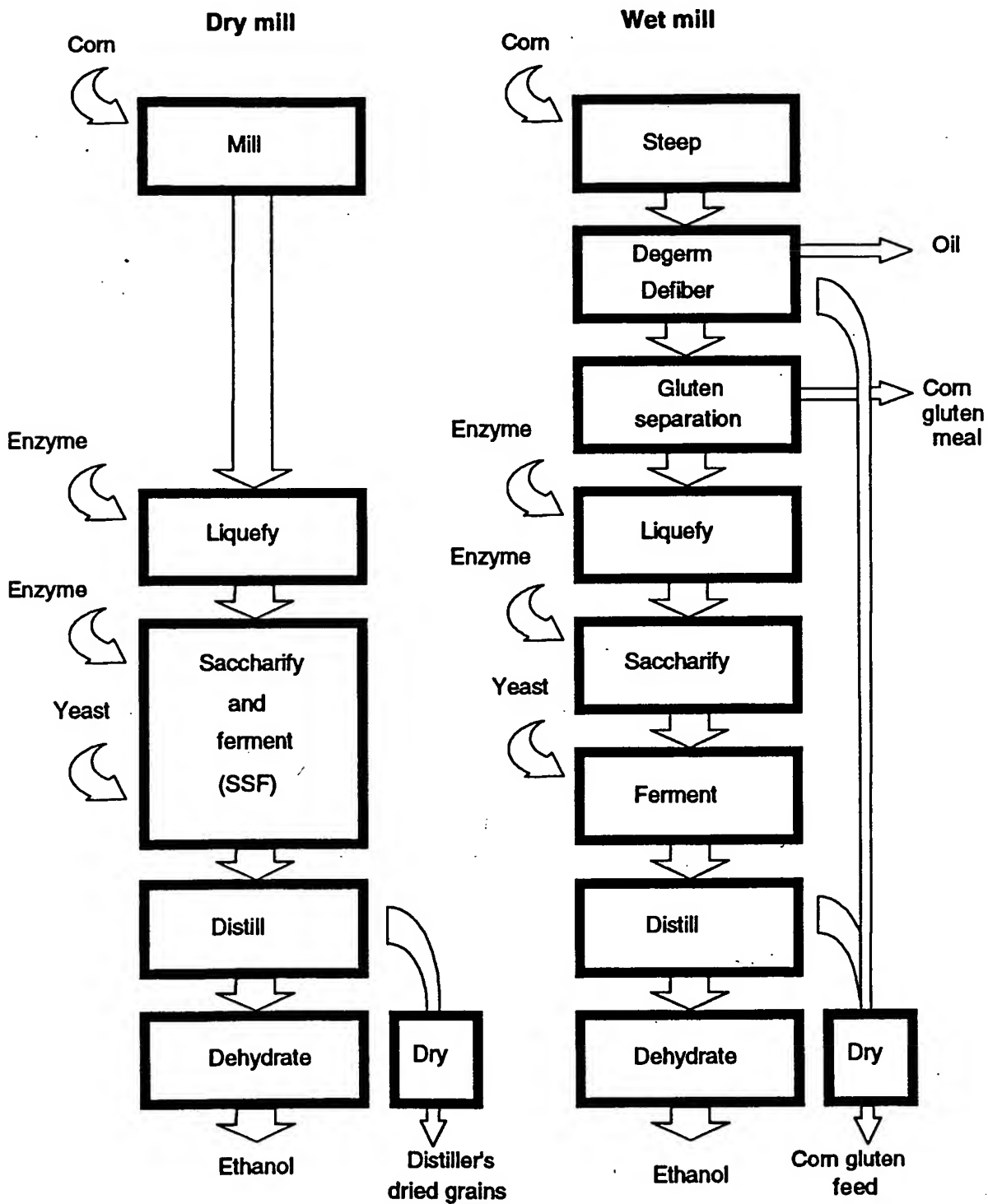
### **Feedstock Costs**

Feedstock cost is a measure of the net cost of the grain from which ethanol is produced. The net corn cost is the difference between the cost of corn and the total revenues received from the sale of coproducts. Over the past 10 years, the net corn cost has been volatile, ranging from 10 to 67 cents per gallon of ethanol. This volatility is mainly due to the large swings in the price of corn, but changes

Figure 1

### Flowchart of wet- and dry-milling

*Wet-milling separates grain into its components before fermentation, raising costs but increasing production of high-value coproducts.*



in coproduct prices have also contributed. Average net corn costs (1981-91) have been 44 cents per gallon of ethanol in a wet mill and 53 cents per gallon in a dry mill. Lower net feedstock costs can be achieved by either lowering the costs of corn or raising the price of coproducts. Technology to lower corn feedstock costs is chiefly aimed at raising the value of coproducts.

### Capital Costs

Another component of producing ethanol is capital costs, which include plant modifications, replacement of worn equipment, and a rate of return on the initial investment. The cost of building a new wet-milling plant (excluding energy generation facilities) with an annual production capacity of 100 million gallons is \$200-\$300 million (LeBlanc and others, 1988), or \$2-\$3 per gallon of annual capacity. The cost of building a dry-milling plant is considerably less because the capital-intensive steps of steeping, degerming, and defibering are not performed. The estimated capital cost of \$0.43 to produce a gallon of ethanol in a state-of-the-art plant (table 1) is based on an initial investment of \$2.25 per gallon of annual capacity and a 15-percent rate of return to investors.

In both dry-milling and wet-milling plants, high capital costs are associated with steps where the process slows or requires special equipment (fig. 2). For example, the steeping step in wet-milling requires large containing vats to ensure sufficient flow to the next stage. Technological innovations that speed up the process or replace expensive equipment are therefore likely to lower capital costs. The total value of capital equipment in a wet-milling plant is higher than in a dry-milling plant. The primary capital expenditure in a wet-milling plant, which accounts for the sizable cost differences, is recovery equipment for removing the germ, oil, and fiber from the corn kernel. In dry-milling plants, nearly half of capital expenditures are for equipment to process coproducts.

### Operating Costs

Operating costs constitute the final component of production costs and include energy, enzymes, labor, management, taxes, and insurance. Many technological innovations have focused on reducing operating costs by raising the efficiency of inputs,

Table 1--Average ethanol production costs<sup>1</sup>

Cost category	Cost
	<i>Dollars/gallon</i>
Feedstock <sup>2</sup>	0.44
Capital <sup>3</sup>	.43
Operating	.37
Total <sup>4</sup>	1.24

<sup>1</sup> A state-of-the-art wet-milling plant with cogeneration of steam and electricity and energy-efficient dehydration. Most ethanol output (1992) is from such plants.

<sup>2</sup> Net corn costs are based on industry average net corn costs, 1981-91. Coproduct credits are reported in the *Sugar and Sweetener: Situation and Outlook Reports*.

<sup>3</sup> Capital and operating costs are updated from LeBlanc and others (1988) and verified with industry sources.

<sup>4</sup> The estimated cost of production of ethanol is \$1.08-\$1.95 per gallon (see U.S. Department of Energy and others, 1992). The lowest cost figure may, however, be difficult for producers to achieve because the final cost depends on the prevailing corn price, and because savings in one area, such as capital costs, may come at the expense of savings in another area, such as energy.

Source: Industry contacts (see list of Individuals and Organizations Contacted).

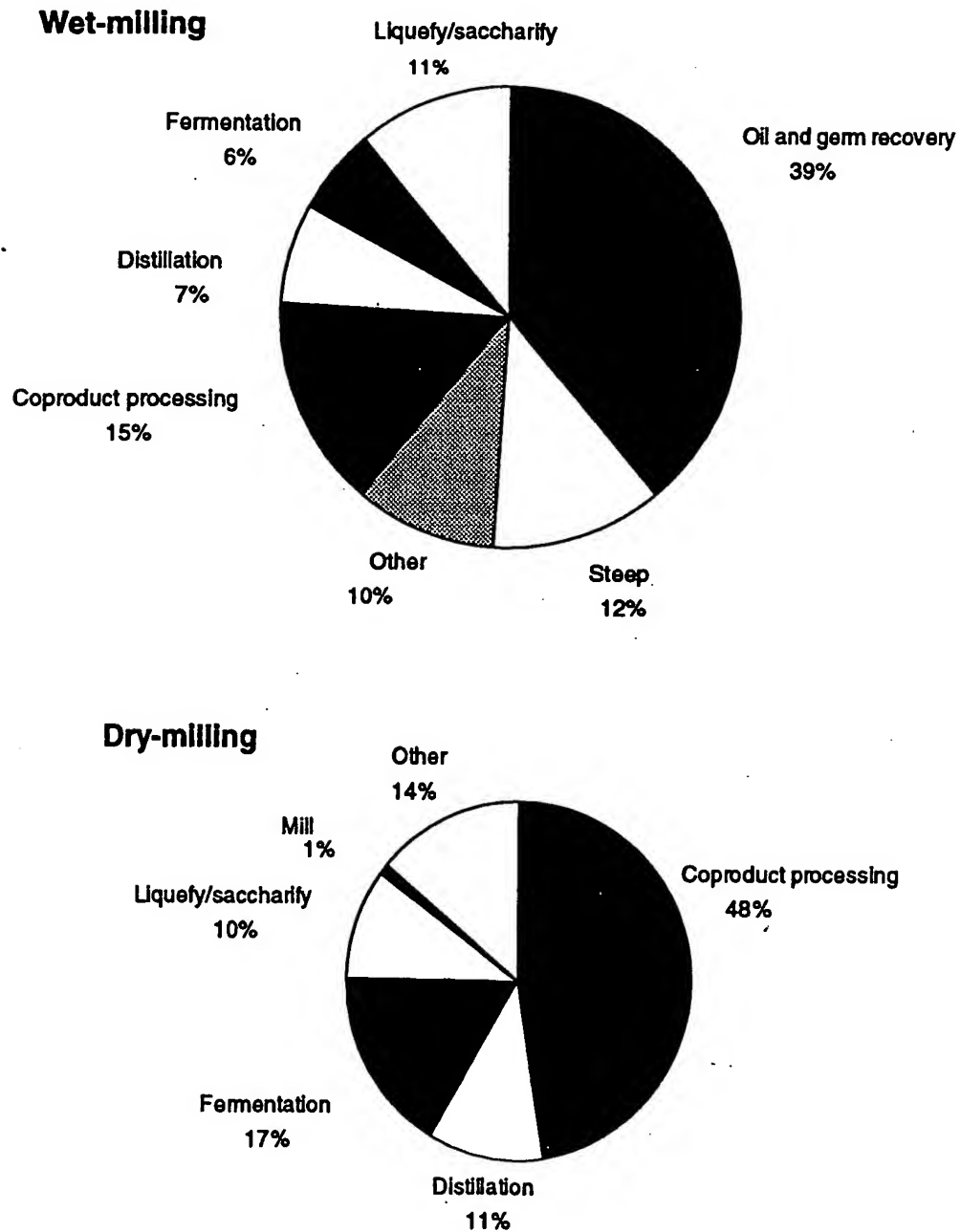
particularly energy. Energy is the greatest operating cost, so innovations that conserve energy have been among the first adopted in the industry, and have accounted for most of the savings in the last 5 years. Most large ethanol plants now receive steam and electricity at low cost from cogeneration facilities that simultaneously produce both. The industry also has reduced energy costs by adopting more efficient means of alcohol dehydration. Lower membrane costs and improved technology may make pervaporation (the use of a semipermeable membrane) an economical option. However, large savings in energy costs are not likely because the present level of efficiency is close to optimal.

The second largest operating cost is the cost of yeast and enzymes. Although these costs have fallen considerably in the past few years, particularly for enzymes, research may further lower the cost of propagating these organisms or reduce the volume needed. Many plants now use computers to control the production processes, reducing supervision and lowering labor costs.

Figure 2

**Capital costs for wet- and dry-milling plants**

*Wet-milling equipment is more costly than that for dry-milling due to more extensive recovery of high-value coproducts (including oil and germ recovery).*



Note: Sizes of pie charts reflect total capital costs.  
Source: Kelm, 1984.



An additional source of savings from technological innovations is improvement in the yield of ethanol.<sup>5</sup> Potential yield improvements could come from more complete conversion of starch to sugar and fermentation of the sugars, more efficient recovery of the ethanol, or the conversion of currently unavailable portions of the feedstock. As yields rise, each gallon of ethanol may be produced from a smaller amount of feedstock, with lower capital investment and lower operating expenses. Therefore, even small improvements in yields create substantial savings in overall costs.

### **Production Cost Savings from New Technologies**

A variety of cost-saving innovations will be available to the ethanol industry for use in the next 2-5 years. Adoption of these innovations, however, depends on an expanding industry that invests in new capital equipment. An estimate of the total cost savings of a new 1996 plant, employing a likely combination of these innovations, over a present state-of-the-art plant is 5.4-7.3 cents per gallon of ethanol produced. In the longer term, still more innovations are likely to move from experimental stages to the plant. In the long term (5-10 years), further cost-saving technologies may save an additional 3.5-8.1 cents per gallon (table 2).

### ***Assessment of Near-Term Technologies***

Innovations likely to be adopted in the near term by the ethanol industry focus on speeding the process time and lowering operating costs (fig. 3). The high estimate for each innovation is a technical upper limit to possible cost savings; the low estimate is based on industry sources (see list of Individuals and Organizations Contacted).

**Gaseous injection of sulfur dioxide and the use of special corn hybrids.** The application of sulfur dioxide (SO<sub>2</sub>) in gaseous form and the use of corn hybrids that have shorter steeping times greatly reduce the time corn must spend steeping in large tanks. This time savings means smaller or fewer tanks will be needed to produce the same amount of ethanol. New plants that adopt gaseous injection may save 1.3-1.7 cents per gallon of ethanol in capital costs when refinements to the process are completed.

Special corn hybrids also shorten steeping time, but are expected to sell at a premium to the type of corn normally used in wet-milling. With an assumed 2-cent-per-bushel premium, use of special hybrids could save 1-1.8 cents per gallon in capital costs. These capital cost savings are available only in a new wet-milling plant because older plants have already invested in steeping tanks and dry-milling does not involve the steeping step.

**Membrane filtration.** Another source of savings in capital costs is a shortening of fermentation time, which allows the use of smaller fermenters. One experimental fermenter design (Simms and Cheryan, 1992) would allow water and ethanol to penetrate a membrane, while trapping the starch and yeast in the fermenter. With the yeast retained, fermentation can proceed continuously at a fraction of the conventional 40-50 hours. As the fermentation time decreases, however, the concentration of the ethanol also decreases. Energy costs per gallon of ethanol rise because more energy is required to distill a more dilute ethanol solution. Nonetheless, with efficient distillation, continuous fermentation with membranes could produce significant capital cost savings for a new plant in the near term.

Membranes also are likely to be used in the saccharification stage to retain enzymes and starch, while allowing glucose and water to pass through. By reducing saccharification time in wet-milling to 10-15 hours and enzyme requirements by a factor of 10, this process could reduce operating costs by 1.2-1.5 cents per gallon of ethanol and achieve small capital cost savings in a new plant. Many wet mills are expected to install membrane systems in the saccharification step because of operating cost savings.

The development of low-cost reliable membranes may allow many plants to recover high-value coproducts and lower operating costs at many points in the production process. The energy and equipment needed to dry the coproducts could be significantly reduced by running liquid components through a microfiltration unit to absorb excess water. High-value coproducts such as lactic acid may also be recovered and concentrated through a system of membranes. The use of membranes gives plants a greater degree of control over the

**Table 2--Model plants of 1996 and 2001 and associated production cost savings**

*Bold type below shows technologies not currently used commercially, but expected to be adopted during the phase indicated.*

Model plant of 1996 (near-term technology)	Model plant of 2001 (long-term technology)
<b>Innovations</b> Cogeneration Steeping with gas injection of sulfur dioxide Membrane saccharification Fermentation: High-tolerance yeast Yeast immobilization Dehydration: Azeotropic distillation Corn grits adsorption	<b>Innovations</b> Cogeneration Steeping with gas injection of sulfur dioxide Membrane saccharification Fermentation: High-tolerance yeast Yeast immobilization Bacterial fermentation Dehydration: Azeotropic distillation Corn grits adsorption Pervaporation Cellulosic conversion of corn fiber
<b>Cost savings over present<sup>1</sup></b> Feedstock <sup>2</sup> \$0.010 - \$0.014 Operating        \$0.025 - \$0.032 Capital <sup>3</sup> \$0.019 - \$0.027 Total             \$0.054 - \$0.073	<b>Cost savings over present</b> Feedstock        \$0.010 - \$0.047 Operating        \$0.027 - \$0.034 Capital           \$0.052 - \$0.073 Total             \$0.089 - \$0.154

<sup>1</sup> The high estimate for these combinations of technologies is based on the technical upper limit to possible cost savings from individual technologies; the low estimate incorporates more practical obstacles to implementation, and is probably more realistic.

<sup>2</sup> Savings from coproduct development are potentially large but speculative, so are not included.

<sup>3</sup> Older plants will be unable to take full advantage due to previously purchased capital equipment.

production of alcohol and allows a greater degree of separation among the various parts of the product stream. These benefits may reduce operating costs at many segments of the plant and curtail capital costs for plants designed to include membrane systems.

**Other improvements.** Another method of lowering operating costs is the improvement of the fermenting organism. The development of yeasts that can work in higher ethanol concentrations (Maiorella and others, 1984) could lower the energy costs of distilling alcohol by 0.8-1.2 cents per gallon of ethanol.

One alternative fermenter design could raise ethanol yields during the fermentation step. This design

immobilizes yeast in beads suspended in a gel. A continuous stream of glucose is fermented as it passes through the gel (Nagashima and others, 1984), speeding the fermentation process and raising ethanol yields. If these yield increases are realized in a new plant, total cost savings will be 2.0-2.7 cents per gallon of ethanol. Although problems with sustaining yeasts while immobilized remain, yeast immobilization reactors should be available in the near term.

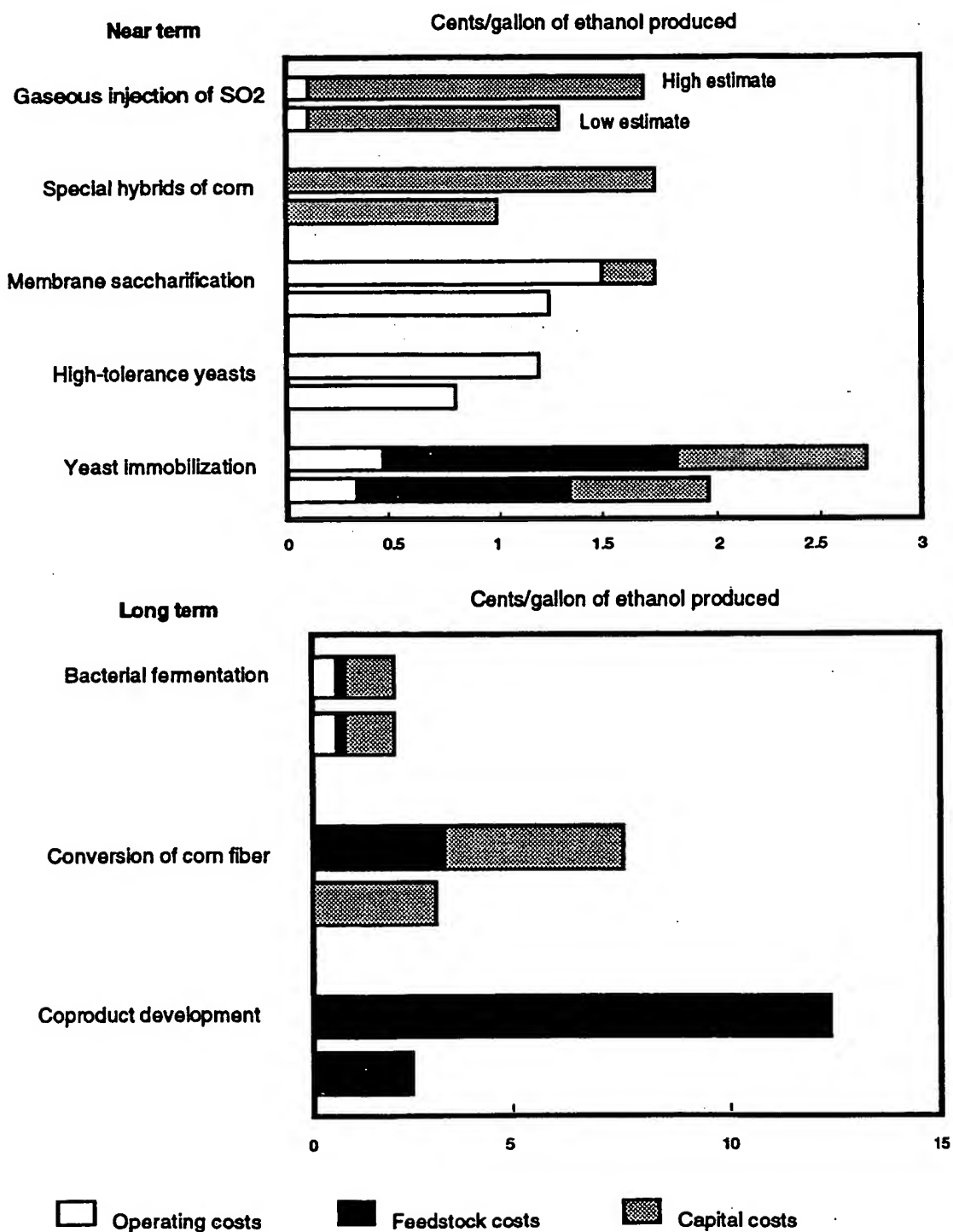
#### **Assessment of Long-Term Technologies**

Technologies that may be incorporated into plants in 5-10 years include bacterial fermentation, conversion of corn fiber to ethanol, and coproduct development (fig. 3). While bacterial fermentation is expected to

Figure 3

# **Production cost savings from new technologies, near and long term**

*High estimates reflect maximum savings that can be achieved in theory.  
Low estimates reflect more likely practical savings to be realized in real-world applications.*



Source: Estimates are based on industry and academic sources. See list of Individuals and Organizations Contacted.

reduce feedstock costs, its primary contribution will be in savings on capital equipment. Conversion of corn fiber will save on capital equipment and also contribute to feedstock savings. Coproduct development will lower net feedstock costs by raising the value of coproducts.

**Bacterial fermentation.** A possible substitute for improved yeast is a wholly different fermentation organism. The bacterium *Z. mobilis*, in laboratory testing, has quickened fermentation, raised alcohol yields slightly, and allowed fermentation at higher temperatures (Busche and others, 1991). Production cost savings from such performance could be as high as 2 cents per gallon. Most of the reduction would be in capital costs because the savings from reduced capacity requirements per bushel of feedstock would outweigh the cost of the new equipment needed (Texeira and Goodman, 1991). Less cooling would be required, reducing energy costs, and some feedstock savings would result from greater conversion efficiency. The *Z. mobilis* bacteria are less stable than yeast and more sensitive to changes in pH and temperature, but these problems may be overcome in the next 5 years.

**Conversion of corn fiber to ethanol.** Current ethanol recovery is approaching the theoretical limit available from the starch portion of the kernel. Converting the hull and other fiber portions of the kernel into ethanol could raise ethanol yields from 2.6 to nearly 3 gallons per bushel. At the same time, the quality of the feed coproduct would improve because, due to fiber loss, the protein content would be higher. The quantity of feed coproducts, however, would fall. Problems may also emerge in drying the coproducts without the fiber acting as a binder for the other components.

Conversion of corn fiber is likely to lower feedstock costs and capital costs. Net corn costs would be reduced by raising both ethanol yield and the value of the coproduct. Capital costs are lower because of higher yields, even though fiber conversion requires unique capital equipment and an increase in distillation capacity. Total savings are expected to be 3-7.5 cents per gallon.

**Coproduct development.** Coproduct sales are potentially the most profitable area of research. The value of ethanol is closely tied to the price of other energy sources, the price of the feedstock is largely

dictated by its alternate uses, and production cost reductions are limited by the physical processes involved in the conversion to ethanol. Revenues from coproducts are not bound by these restrictions.

Some research on coproduct recovery focuses on using semipermeable membranes to remove small quantities of valuable products from the corn-refining stream. One such coproduct is lactic acid, produced unintentionally during fermentation. (In the long run, however, it may prove more economical to produce lactic acid in a separate fermentation.) High-value, low-volume coproducts, such as citric acid or sorbitol, may be removed as more sophisticated membrane technology becomes available.

Coproduct research also focuses on high-value uses of carbon dioxide, produced in quantities almost equal to ethanol, but currently sold for less than 1 cent per pound. Researchers have discovered a bacterium that converts carbon dioxide and hydrogen into acetic acid (Wood, 1991). Converting the carbon dioxide from the production of a gallon of ethanol into acetic acid is estimated to cost around \$0.75 and produce about 4.3 pounds of acetic acid, which at current prices would sell for more than \$1.50. If acetic acid were produced on a large scale, its price would probably fall, but this process illustrates, nonetheless, the potential for achieving sizable savings through the further development of coproducts. There are several other possibilities for industrial use of carbon dioxide (Myers, 1992). It is difficult to predict which coproducts will eventually emerge as most profitable, but in the long term, savings from all of them could be as large as savings from plant innovations.<sup>6</sup>

### Industry Expansion

A great deal of additional production can be coaxed out of existing facilities. However, for production to increase sufficiently to meet the demand for oxygenated (cleaner burning, as stipulated by the Clean Air Act) fuels, much of the increase will have to come from newly constructed facilities. New plants will be able to employ new technology more easily than older plants, improving the industry's overall efficiency. The older plants will be limited to "plug-in" or modular technologies that do not require redesigning the entire plant.

To take advantage of economies of scale, new wet-milling facilities will probably have an annual capacity of at least 100 million gallons. Building new facilities will introduce state-of-the-art technologies at a faster rate than they have been adopted in the past. This acceleration will improve the industry's overall efficiency.

Economies of scale for dry mills may begin to level off at about 50 million gallons of annual capacity. Dry mills can be built economically on a smaller scale and fit operations that can feed the coproduct to livestock without drying. Increases in other niche markets are also possible. Lactose from cheese whey, for example, has been successfully fermented to ethanol, solving a disposal problem and adding to the product line at the same time.

### **The Conversion of Biomass into Ethanol**

A jump in ethanol production through the conversion of corn kernels is likely to be constrained by a number of factors: the relatively high cost of corn, which has many alternate uses; limited markets for coproducts such as corn gluten feed and dried grains and solubles; and competition for land suitable for corn cultivation. A doubling of ethanol production from corn would require approximately 350 million additional bushels of corn each year, putting upward pressure on the price of corn and doubling the supply of coproducts. Other food crops considered as a feedstock for ethanol production, such as potatoes and sugarcane, are also expensive because of their high value as human food products. These restrictions do not apply, however, to the organic material called biomass, which is available as a byproduct of agricultural production and as a waste material.

Biomass includes agricultural residues, waste streams from agricultural processing, municipal solid wastes, yard and wood wastes, and crops grown expressly for their energy content. These materials cost much less than corn and are more abundant. Conversion of waste materials and agricultural residues into ethanol could produce up to 3.8 quads (1 quad =  $10^{15}$  Btu) of energy each year. Crops grown expressly for energy content on excess cropland could annually produce 11.4 quads of energy. Together, these sources of energy would account for half of the total annual consumption of

energy in the U.S. transportation sector (Lynd and others, 1991).

### **Technological Barriers and Opportunities**

Technology for converting biomass into ethanol has until recently been unproven and too costly for commercial-scale ventures. Although simple sugars are ultimately fermented to form ethanol from both corn and biomass feedstocks, the sugars in biomass are more tightly bound in long chains, and some simple sugars are different from the sugars in corn. A kernel of corn is composed primarily of starch, which is readily reduced into glucose, a sugar that can be efficiently fermented by yeast into ethanol. Most biomass is composed of cellulose, hemicellulose, lignin, and ash. The cellulose and hemicellulose fractions are made up of long chains of six-carbon sugars (glucose) and five-carbon sugars. The cellulose portion ranges from 30 to 50 percent of total weight, hemicellulose from 25 to 35 percent, and lignin from 10 to 30 percent, depending on the feedstock. Lignin cannot be converted into ethanol, but can serve as an energy source and combustible fuel for the conversion of cellulose and hemicellulose into ethanol.

A biomass conversion plant would differ from the conventional wet or dry mill first in the prehandling and sorting steps (fig. 4). These steps vary considerably depending on the biomass feedstock. For example, processing municipal solid waste requires a more complicated and costly sorting procedure than processing agricultural residues. The biomass conversion process also varies from conventional corn processing because of the need to break down cellulose and to ferment five-carbon sugars.

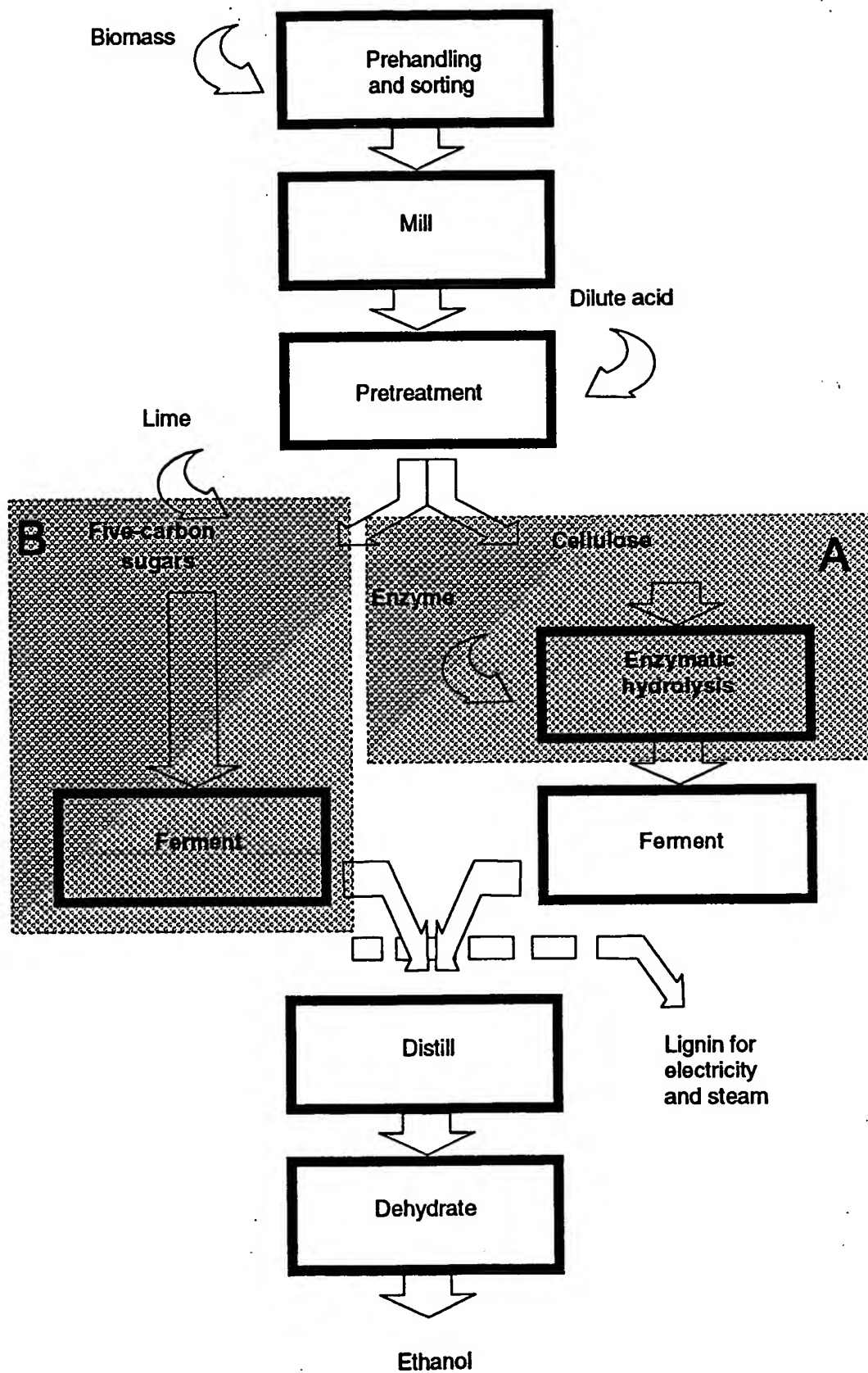
After sorting, the feedstock material is ground in a mill and goes to the pretreatment stage where dilute acid is used to break down the hemicellulose into five-carbon sugars. The five-carbon sugars are then fermented separately. The cellulose is broken down into glucose through enzymatic hydrolysis before being fermented in the usual way. Lignin is a byproduct of biomass conversion that has potential industrial uses. Current plant designs use lignin as a source of electricity and steam.

The two technological barriers to biomass conversion have been the lack of an efficient

Figure 4

# Flowchart of yard waste biomass processing plant

*Biomass conversion requires a separate process to break down complex five-carbon sugars.*



method for hydrolyzing (converting) cellulose into glucose and the lack of an effective organism for fermenting five-carbon sugars. Although both corn starch and cellulose are composed of chains of glucose, the complex structure of cellulose makes the complete separation of all the glucose molecules extremely difficult. Concentrated mineral acids, such as sulfuric acid, have been used to break the bonds between glucose molecules. The hydrolysis of cellulose through the use of acids, though rapid and efficient, also has significant drawbacks. Acid hydrolysis requires expensive containment and recovery systems to keep acid costs and equipment corrosion to a minimum. Furthermore, the highly reactive nature of acid hydrolysis reduces some glucose into useless and possibly toxic byproducts.

An alternative process combines a chemical pretreatment of cellulose with an enzymatic hydrolysis (fig. 4, area A). Enzymes capable of hydrolyzing cellulose are produced in large quantities from microbial sources. The enzymes, which act as catalysts, operate slowly and have been more expensive than acids. On the other hand, glucose yields from enzymatic hydrolysis can approach 100 percent of the theoretical yield, and advances in genetic engineering promise to lower the cost of enzymes. When enzymatic hydrolysis is employed after a pretreatment step, the hydrolysis and fermentation stages of ethanol production can be combined. This process, another form of SSF, raises productivity by allowing the fermenting organisms to consume simple sugars such as glucose as soon as they are separated by the enzymes. Enzymatic hydrolysis appears to be the process through which the goal of cleanly and cheaply converting cellulose into glucose is most likely to be achieved.

The remaining technical barrier to biomass conversion has been the lack of an organism to ferment the five-carbon sugars that result from the hydrolysis of hemicellulose (fig. 4, area B). Unlike cellulose, hemicellulose hydrolyzes easily with a mild pretreatment into a variety of five-carbon sugars. Common strains of yeast, however, either cannot ferment five-carbon sugars or cannot tolerate high concentrations of ethanol. The inability to convert such a large portion of biomass into ethanol makes production economically infeasible. Advances in genetic engineering, however, have largely overcome this barrier. Genes that instruct

other organisms to ferment both five- and six-carbon sugars have been introduced into *E. coli*, a bacterium present in the human digestive system. The resulting organism is capable of fermenting both glucose and five-carbon sugars with a high productivity and with fermentation yields that match those of common yeast strains (Ingram and others, 1991). Further genetic improvements to fermenting organisms may reduce enzyme requirements for the hydrolysis of cellulose and raise fermentation yields.

A number of problems for biomass conversion remain. Pretreatment systems must be developed that economically allow high yields of sugar during hydrolysis. Also, because biomass feedstocks are much more diverse than those for corn-derived ethanol, the effects of heterogeneous feedstocks must be closely examined. Finally, it must be demonstrated that the fermenting organisms are stable during fermentation and environmentally benign.

### Costs of Production

The technology for converting biomass into ethanol is at a stage in which working production plants are being designed for near-term construction. Operating and capital costs for prospective biomass conversion plants (table 3) are not much higher than operating and capital costs for very large and efficient wet- and dry-milling plants. Biomass conversion plants are assumed to have optimized production parameters based on the experience of earlier plants of similar design; costs are typical of fifth or tenth plants, rather than of the first pilot plant. No biomass conversion plant has been constructed yet, so cost estimates are speculative. Also, biomass provides its own energy source for ethanol conversion in the form of lignin, which can be burned in a boiler to provide steam and electricity, reducing costs relative to corn conversion. Both biomass conversion plants (table 3) are capable of providing all their power using lignin and even generating an electricity credit if access to local utilities is available. Energy expenditures are the largest operating cost in wet- and dry-milling plants.

Finally, biomass conversion plants will differ from corn wet- and dry-milling plants in the front end of the plant, where sugars are extracted from different feedstocks. Biomass is a relatively bulky feedstock,



**Table 3--Cost estimates for two biomass conversion plants**

Cost category	Plant 1 (10 million gallons/year)	Plant 2 (60 million gallons/year)
<i>Dollars per gallon</i>		
Operating costs	0.481	0.339
Labor	.087	.027 <sup>1</sup>
Fuels	.012	— <sup>2</sup>
Nutrient, boiler chemicals, acid	.100	.141
Enzymes	.115	— <sup>3</sup>
Supplies and materials	.035	— <sup>4</sup>
Maintenance	.058	.066
Overhead	.035	.072
Tax and insurance	.039	.033
Capital cost	.390	.484 <sup>5</sup>
Operating and capital costs	.871	.823
(Electricity credit)	N.A.	-.071
(Waste disposal cost)	N.A.	-.007

N.A. = Not available.

<sup>1</sup> Lower cost is a result of economies of scale (compared with plant 1).

<sup>2</sup> Power provided by lignin, produced during biomass conversion.

<sup>3</sup> Plant 2 produces enzymes for the hydrolysis of cellulose.

<sup>4</sup> Included in the nutrient, boiler chemicals, acid category.

<sup>5</sup> Higher productivity due to faster rates of reaction lowers cost in plant 1, while enzyme-producing equipment raises cost in plant 2.

Source: Costs for plant 1 are obtained from Bioenergy International and for plant 2 from the National Renewable Energy Laboratory.

so a conversion plant requires an extensive handling facility for processing delivered biomass into a usable form. Some feedstocks require more processing than others. Extensive sorting and filtering is required to separate the fermentable portion of municipal solid waste from recyclable materials such as glass and steel. The simpler processing of corn stover (dried stalks), on the other hand, resembles the dry-milling of corn, in which a hammer mill reduces the size of the feedstock. Although the bulk of biomass raises handling costs, the conversion of biomass into ethanol is nearly total and eliminates the substantial cost of drying and handling coproducts such as corn gluten feed and dried grains and solubles. Biomass conversion

plants, however, lack the flexibility of a wet-milling plant to produce high-fructose corn syrup when not producing ethanol.

Although operating and capital costs for an efficient biomass conversion plant are slightly higher than typical costs for corn-processing plants, feedstock costs may be dramatically lower. Feedstock costs for some wastes that are expensive to dispose of, such as municipal solid waste and yard waste, may even be negative. That is, municipalities may be willing to pay ethanol producers to take the waste. The payments are called tipping fees. The primary cost for most wastes and residues is collection and storage, as well as any necessary pre-plant processing. For example, one estimate of the cost of using corn stalks for ethanol production is 20 cents per gallon of ethanol, including a price for the material, the cost for removing and stacking stalks, and the cost of transportation (Gerber, list of Individuals and Organizations Contacted). Before low feedstock costs are likely to give an advantage to individual biomass conversion plants, however, a steady supply of biomass must be ensured and an infrastructure must be developed for harvesting, storing, and transporting.

### Industry Development

Feedstock characteristics account for the greatest differences between the biomass conversion industry and the corn conversion industry. Because biomass is bulkier than corn and the infrastructure for its handling less well developed, biomass conversion plants are initially likely to be small, with a capacity of 10-50 million gallons of ethanol per year. Construction of plants that can convert municipal lawn and yard waste into ethanol may begin in the next 5 years. Corn wet-milling and dry-milling plants may also begin to convert the fiber portions of their feed coproducts into ethanol, depending on the value of the new, higher quality coproduct. Plants to convert municipal solid wastes and agricultural residues into ethanol would also emerge in the longer run. The variety of biomass feedstocks and small size of conversion plants should involve a wider variety of participants than in the corn ethanol industry, including local governments, farmer cooperatives, and small businesses. Marketing ethanol will be more difficult at this smaller level, but lower production costs may afford openings to these firms.



## **Conclusions**

Technological innovations in converting corn to ethanol will likely lower all three components of production costs: feedstock, operating, and capital costs. In the near term, the adoption of innovations in new facilities will result in lower equipment costs, lower ingredient costs, and slight ethanol yield increases over current plants. Cost reductions of 5-7 cents per gallon are likely in the near term (by 1996). Older plants, having already invested in equipment, will be unable to take full advantage of capital cost savings, but can still save 3.5-5 cents per gallon.

In the long term (by 2001), a state-of-the-art corn conversion plant could reduce costs further by improving fermentation processes and converting a portion of its coproducts into ethanol through the conversion of corn fiber. Adding these technologies to a new plant will increase cost savings to 9-15 cents per gallon (7- to 11-percent savings over the cost of production in a current state-of-the-art plant). The innovations discussed in this report apply to most of the steps in the production process where significant savings are possible. Additional cost savings may result from incremental improvements to production efficiency or unexpected breakthroughs, but are likely to be small relative to the projected savings, especially in the near term.

The cost of producing ethanol will also be greatly influenced by technological advances other than innovations in the plant. Farm technologies that raise corn yields or lower input costs may lower feedstock costs for ethanol production. Refinements and new, higher value uses for coproducts are an even likelier source of new revenues for producers and could reduce the cost of ethanol by as much as plant innovations.

By the turn of the century, biomass-derived ethanol may begin to complement ethanol derived from corn. The conversion of biomass into ethanol greatly increases the supply and variety of feedstocks available for ethanol production. Operating and capital costs for biomass conversion plants are comparable to combined costs at corn conversion plants. Feedstock costs can be distinctly lower. Technical barriers to economical biomass conversion, however, still exist and lower cost levels may be achieved only after pilot plants are constructed and the production process is refined.

The use of ethanol as a fuel supplements imported oil as a domestic renewable resource with some environmental benefits. Because of the relatively high costs of production, however, the production of ethanol is supported by government incentives. Cost reductions from the new technologies will move the industry somewhat nearer competitiveness without incentives.

## Endnotes

1. The energy required to produce 1 gallon of ethanol (43,000 Btu) is less than the energy contained in a gallon of ethanol (78,000 Btu).
2. Hybrid techniques that use elements of both wet- and dry-milling exist and may be used more in the future.
3. Each bushel of corn that enters the wet-milling process yields approximately 13.5 pounds of CGF, 2.65 pounds of CGM, 1.55 pounds of corn oil, and 2.5 gallons of ethanol. The dry-milling process produces an average 17.5 pounds of distiller's dried grains plus solubles (DDGS) and 2.6 gallons of ethanol. Higher ethanol yields are documented in some dry mills, where DDGS yields can be as low as 16 pounds per bushel.
4. The final dehydration can be accomplished through (1) azeotropic distillation using benzene or another azeotrope, (2) a molecular sieve, (3) a corn grits sieve, or (4) pervaporation, the use of a semipermeable membrane.
5. A bushel of corn weighing 56 pounds yields about 34 pounds of starch (Ladisich, 1987; Lawford, 1988). Starch converted to glucose with perfect efficiency would yield approximately 37.4 pounds of fermentable sugar in hydrous form. If the sugars were then fermented with perfect efficiency and all the water removed with no ethanol loss, the result would be about 2.85 gallons of fuel-grade ethanol. If the fiber portion of the kernel were converted as well, an additional 0.3 gallon might be produced. However, industry averages are less than 2.6 gallons of ethanol per bushel of corn.
6. Coproducts from the fermentation of five-carbon sugars, which are present in the hemicellulose portion of grasses, wood fibers, and even corn hulls, afford an even wider range of recoverable coproduct possibilities (Tsao, Ladisich, and Bungay, 1987). Agricultural Research Service scientists estimate that savings of 13-18 cents per gallon are possible through coproduct development in the next 3-5 years.

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# The U.S. corn ethanol industry: An overview of current technology and future prospects

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## Abstract

Last year, 1.77 billion gallons of fuel ethanol were produced in the U.S., over 90% of which was produced from corn. Ethanol demand is expected to more than double in the next several years as it is used to replace the fuel oxygenate, methyl tertiary-butyl ether (MTBE). Corn is prepared for ethanol fermentation by either wet milling or dry grinding. Most newly constructed ethanol plants use dry grinding because of its lower capital costs. However, corn wet millers have also expanded production by adding on to existing plants. Current technology allows for 2.5 (wet milled) to 2.7 (dry grind) gal of ethanol per bushel of corn. An opportunity exists for increasing this yield by also converting the fibrous components of the corn kernel (i.e. pericarp and germ) to ethanol. Fermenting these non-starch fractions could increase the yield from a bushel of corn by a maximum of 10%. In this brief review, the economic and technical aspects of ethanol production will be explored as well as future prospects for increasing ethanol yield from corn by fermenting the non-starch fractions.

## Introduction

The United States produced 1.77 billion gal of fuel ethanol (2001) and over 90% of it was produced from corn. U.S. ethanol production has expanded dramatically since 1980 (Fig. 1) and today utilizes over 5% of

should continue to increase as individual States phase out the use of methyl tertiary butyl ether (MTBE) as a fuel oxygenate. The California Energy Commission has estimated that production capacity is expected to grow to more than 4 billion gals/yr by 2006 (MacDonald *et al.*, 2001).

The growth in the use of fuel ethanol can be traced to environmental legislation and Federal and State economic incentives. In 1990, the Clean Air Act amendment was passed which required the use of oxygenated fuel and reformulated gasoline to reduce carbon monoxide emissions. The list of available fuel oxygenates

are ethanol, MTBE, and ethyl tertiary butyl ether (ETBE). Several Midwest States mandate the use of ethanol. The Federal government has also encouraged the use of ethanol by exempting it from the federal gasoline excise tax. This tax exemption was set to expire in 2000, but has since been renewed until 2006. Several Midwestern States also introduced further financial incentives for ethanol. These incentives are designed to favor smaller ethanol plants, such as those built by farmer cooperatives. Typical is Minnesota's Tax incentive, which gives 20 cents per gal per year for 10 years for a maximum of 50 million gals per year. Many ethanol plants designed around this incentive have since expanded capacity.

Ethanol demand is expected to increase dramatically over the next several years because of environmental concerns associated with the use of MTBE. MTBE, which has leaked from gasoline storage tanks, has been discovered to be a major ground water contaminant and more resilient to microbial degradation than other common organic water pollutants (Anonymous, 1999). As a result of these findings, California and States located in Eastern United States have

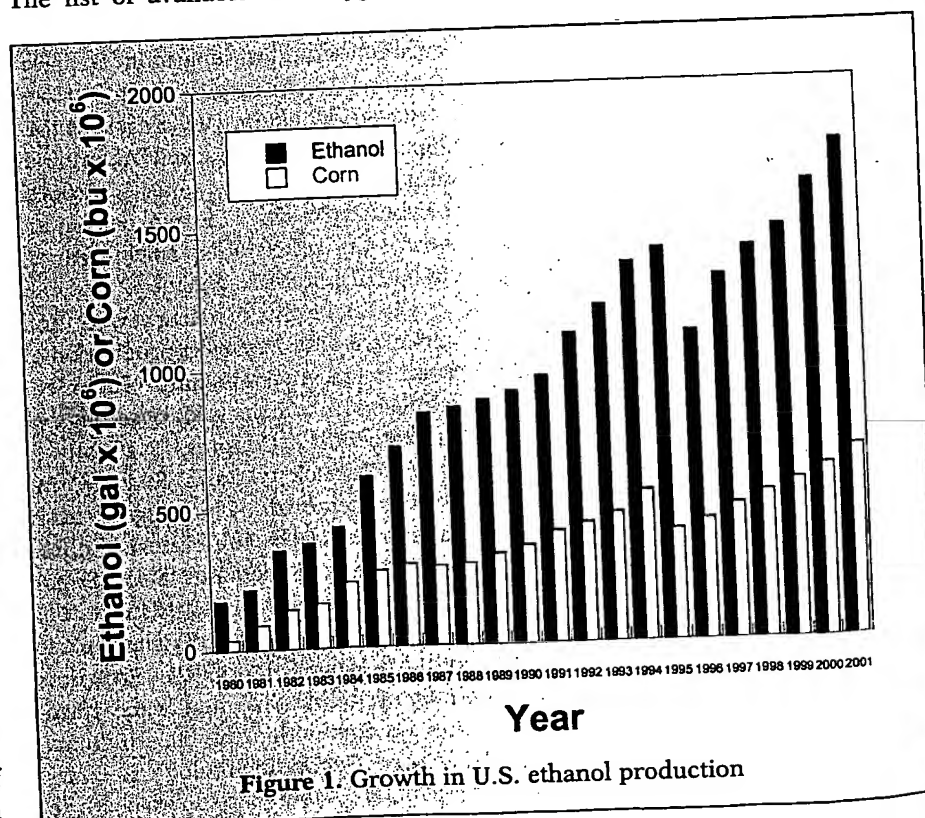
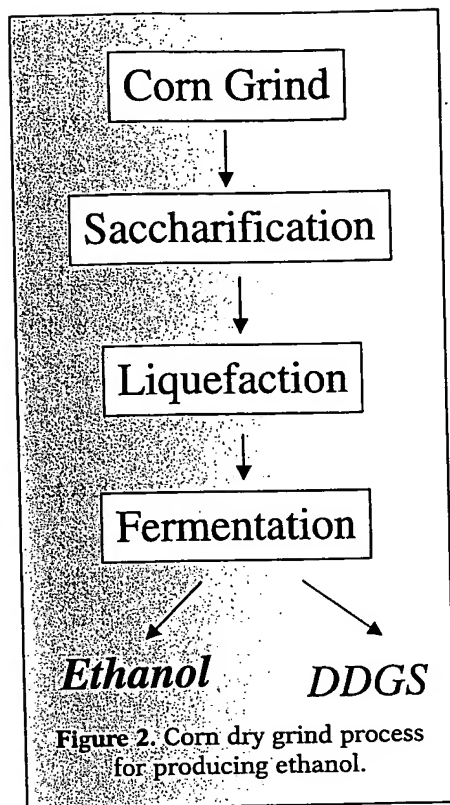


Figure 1. Growth in U.S. ethanol production



indicated interest in phasing out MTBE. In June 2001, the Bush Administration refused California's request for a waiver of the oxygenate fuel requirement, thereby, forcing the use of ethanol if production of MTBE is stopped. The annual California ethanol market is expected to grow by 500 - 800 million gals (McDonald *et al.*, 2001). A possible compromise has recently been worked out in the U.S. Senate. In the proposed National Energy Bill (currently in the U.S. Senate) the oxygenate requirement would be abolished and, instead, a renewable fuels standard established for promotion of ethanol (Brown, 2002). The bill specifies a target ethanol production goal of 5 billion gals/yr by 2012 (*ibid*).

Beyond its use as an oxygenate, proponents of the use of fuel ethanol cite the following benefits: reduces reliance on imported oil, lowers greenhouse gas emissions, and promotes rural development. A study to be published this spring (2002) by the USDA has estimated that ethanol has a 34% net energy balance (Shapouri personal communication, for an older report see Shapouri *et al.*, 1995). Ethanol is available as a 10% v/v (E10) and 85% v/v (E85; only in the

Midwest) blend with gasoline. E10 and E85 lower petroleum use by 6% and 74% per gallon, respectively (Wang *et al.*, 1999). E10 also reduces greenhouse gas emissions by 1% and E85 by 34% (*ibid*). Finally, ethanol is good for rural development by supplying an important market for corn and providing jobs at rurally located ethanol plants. In 1997, it was estimated that fuel ethanol increased farm income by 4.5 billion dollars and led to the creation of 195,200 jobs (Evans *et al.*, 1997).

#### Current ethanol production processes

Corn is processed to ethanol by either dry grinding or wet milling. Last year, for the first time, dry grinding production (55%) exceeded that of wet milling in the U.S. Growth of dry grind mill capacity has exceeded that of wet mills because dry grind mills have lower capital costs. Capital costs for dry grind mills have been estimated at \$1.25-1.50 per gal. In recent times, no new wet mills have been built; instead producers have relied on expanding existing facilities. Descriptions of the dry grinding and wet milling processes follow.

#### Dry grind process

Sometimes the ethanol dry grind process is referred to as dry milling. Dry grind process, however, is the preferred term as it avoids confusion with dry milling corn for production of corn grits and flour. A schematic of a dry grinding process is shown in Figure 2 (for detailed reviews: Jacques *et al.*, 1999; Elander and Putsche, 1996). Corn is hammer milled to pass through a 1/8-3/16 inch screen. If the grits exit the mill too coarse, not all of the starch becomes available for fermentation and if it is too fine, the residual biomass is difficult to separate following fermentation.

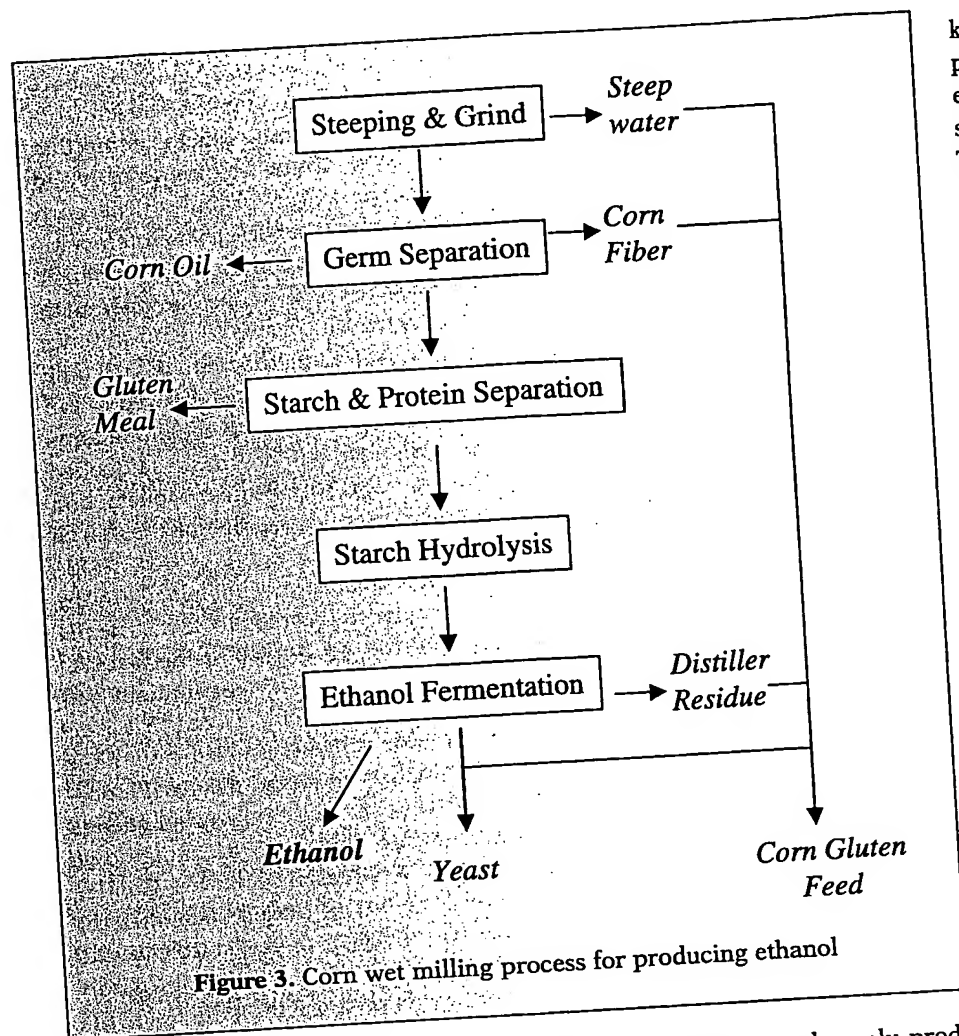
Once ground, the corn is mixed with water to form a mash. The pH of the mash is adjusted to 6.0 with ammonia followed by addition of 1/3 of the alpha-amylase. Alpha amylase is added to begin to break down the starch polymer and produce soluble

dextrins. The mash is heated to above 110°C using a jet cooker. The jet cooker is a special tube reactor/pump that uses direct steam heating to heat and shear the starch granules. The corn mash is kept at the elevated temperature for several minutes by pumping it through a holding tube equipped with a backpressure valve. The mash flows from the holding tube into a flash tank and the temperature is allowed to fall to 80-90°C. The rest of the alpha amylase is added and the mash is liquefied for at least 30 minutes. Liquefaction greatly reduces the size of the starch polymer.

The liquefied mash is placed in the bioreactor and cooled to 32°C. The pH is lowered to 4.5-5.0 using backset (recycled from the distillation column) and phosphoric acid. The fermentation stage is started by adding the glucoamylase and the yeast inoculum. Glucoamylase converts liquefied starch into glucose by breaking down alpha-1,4 glucosidic linkages. Enough glucoamylase is added such that the saccharification of the starch to glucose, which occurs continually through the fermentation, does not limit the rate of ethanol production. In addition, either  $(\text{NH}_4)_2\text{SO}_4$  or urea is added as a nitrogen source for the growth of the yeast. Recently, ethanol dry grind mills have also begun to add proteases that break down the corn protein to a free amino acid, which serve as an additional source of nitrogen for the yeast. The fermentation lasts 48-72 hours and has a final ethanol concentration of 10-12% v/v. The pH of the beer declines during the fermentation to below 4 because of carbon dioxide formed during the ethanol fermentation. The decrease in pH is important for increasing the activity of glucoamylase and inhibiting the growth of contaminating bacteria.

Dry grind plants can reduce the amount of glucoamylase added by saccharifying the liquefied starch at 65°C prior to fermentation. However, plants have gone to SSF (simultaneous saccharification and fermentation) because it lowers the opportunity for microbial contamination. SSF also lowers the initial osmotic stress





of the yeast by avoiding a concentrated glucose solution.

Upon completion, the beer is first distilled through the beer column. The distillate is further concentrated to 95% v/v of ethanol, at which concentration water and ethanol form an azeotrope. The ethanol is brought up to 100% v/v concentration using a molecular sieve bed. Finally, the ethanol is denatured with the addition of fusel oil, higher alcohols produced by the yeast during fermentation, and gasoline. Denaturation is required to avoid the alcohol beverage tax.

The stillage leaving the beer column is centrifuged with a decanter. Between 15 and 30% of the liquid fraction (thin stillage) is recycled as backset. The remainder is concentrated further by evaporation and mixed with the residual solids from the fermentation. The mixture is then dried to 9% moisture in a gas-fired rotary dryer. The final product is marketed as Distiller Dried Grains with

some plants) CO<sub>2</sub> are the only products (Table 1).

Corn accounts for more than 70% of the cost of producing ethanol (McAloon *et al.*, 2001). There is some interest by seed companies to market specific hybrids for ethanol dry grind mills. The authors have recently compared three hybrids and determined that the fermentation efficiency, a measure of ethanol yield per available starch, varied among the hybrids. The significance of this finding is that both starch content and starch availability varies with hybrid. The authors have also compared the fermentation of Bt vs. non-Bt corn and found no differences in ethanol yield or productivity.

#### Wet milling process

Wet mill plants are larger and produce more products than dry grind plants (Table 1; for detailed reviews: Jacques *et al.*, 1999; May 1987). Wet mills separate each component of the corn

kernel: the endosperm, germ, and pericarp (e.g., corn hull). The endosperm is further separated into starch and gluten (protein) streams. The gluten is marketed as gluten meal; a high protein (60%) animal feed used mainly by the poultry industry. Corn oil is extracted from the germ. The pericarp is separated as corn fiber. The corn fiber is combined with the steep liquor and de-oiled germ meal and sold as corn gluten feed, a low protein (20%) animal feed. In addition to producing ethanol, most corn wet millers produce other products from the starch using either enzymatic or fermentation processes. Examples of these products are dextrin, high fructose corn syrup (HFCS), citric acid, amino acids, and lactic acid.

The key to isolating these different corn fractions is steeping (Fig. 3). In the steeping step, the corn is soaked in water and treated with SO<sub>2</sub> (1600 ppm) at 52°C for 20-40 hr. The corn is further acidified by the growth of lactic acid bacteria at later stages during the steep. Steeping swells the kernel and loosens the bonds between the protein and starch in the endosperm. Following steeping, the kernels are shredded in a mill designed to dislodge the germ. The germ, which contains about 30% oil, is then separated based upon its lower density compared to the rest of the kernel with hydrocyclones. The recovered germ is next processed to extract the corn oil, and the residual germ meal is blended into corn gluten feed.

The protein and starch are next separated from the fiber by passing the slurry along metal screens. While the fiber is retained on the screens, the protein and starch pass on through. The fiber is further washed to recover additional starch and finally folded into the corn gluten feed. The protein is next separated from the starch based upon density using disc-nozzle centrifuges. The recovered protein (gluten) is sold as gluten meal. The recovered starch is further washed to remove residual protein. The cleaned starch, if used for ethanol or HFCS production, is enzymatically hydrolyzed to glucose using alpha amylase followed by glucoamylase. As

Table 1. Corn milling product yields and selling prices

Co-Product	Yield (per bushel)	Selling Price (U.S. \$)
<b>Corn Dry Grind Ethanol Fermentation</b>		
Carbon Dioxide	16.7 lb	na
DDGS <sup>1</sup>	16 lb	82 per ton <sup>2</sup>
Ethanol	2.65 gal	1.40-1.50 per gal <sup>3</sup>
<b>Corn Wet Milling Ethanol Fermentation</b>		
Carbon Dioxide	15.8 lb	na
Corn Oil	1.83 lb	0.182 per lb <sup>3</sup>
Corn Gluten Meal	2.60 lb	217 per ton <sup>2</sup>
Corn Gluten Feed	11.2 lb	57 per ton <sup>2</sup>
Ethanol	2.50 gal	1.40-1.50 per gal <sup>3</sup>

<sup>1</sup>Distillers dried grains with solubles

<sup>2</sup>Feedstuff, March 18, 2002 (Chicago prices)

<sup>3</sup>Chemical Market Reporter March 11, 2002 (Midwest Prices)

Table 2. Potential ethanol production from corn fibrous fractions

Biomass	Carbohydrate (% wt/wt)s	Starch (%wt/wt)	Cellulose (%wt/wt)	Xylan (% wt/wt)	Availability (tons per yr)	Ethanol <sup>1</sup> (gal per yr)
Corn Stover <sup>a</sup>	58.4	—	36.4	22	125-200x10 <sup>6</sup>	7.5-12x10 <sup>6</sup>
Corn Fiber <sup>a</sup>	69.6	19.7	14.1	32.4	3.4x10 <sup>6</sup>	385x10 <sup>6</sup>
DDGS	46.5	—	22.8	20.7	3.0x10 <sup>6</sup>	133x10 <sup>6</sup>

<sup>1</sup>Assumes theoretical ethanol yield

<sup>a</sup>Compositional Data: Corn Stover (Wiselogle *et al.*, 1996), corn fiber (Grohmann *et al.*, 1997), DDGS (Miron *et al.*, 2001). Availability Data: Corn Stover (Glassner *et al.*, 1998), Corn Fiber (Anonymous, 2000), DDGS (estimated from U.S. Renewable Fuel Association ethanol data, 2001)

<sup>a</sup>Availability includes all wet milled corn

with dry grinding, a jet cooker is used during the liquefaction step. Separate saccharification and fermentations steps are carried out. To aid in saccharification, pullanase is added with the glucoamylase. The fermentation is often run continuously in a cascade scheme, which reduces the amount of dried yeast needed. Ammonia or urea as well as liquid recovered from the steeping are also added to the fermentation broth. Foaming is often a problem in wet mill fermentations, because the corn oil has been removed, which necessitates the addition of an antifoam agent.

Recently, some corn seed companies have begun marketing hybrids as being superior for wet milling. Traditionally, corn hybrids were evaluated on yield and starch content. Eckhoff *et al.* (1993) developed a method for simulating the wet mill

process in a laboratory. The results have shown that hybrids with similar starch contents can still vary in extractable starch contents (Zehr *et al.*, 1995). The superior hybrids are rated for high extractable starch content.

#### Modified milling processes

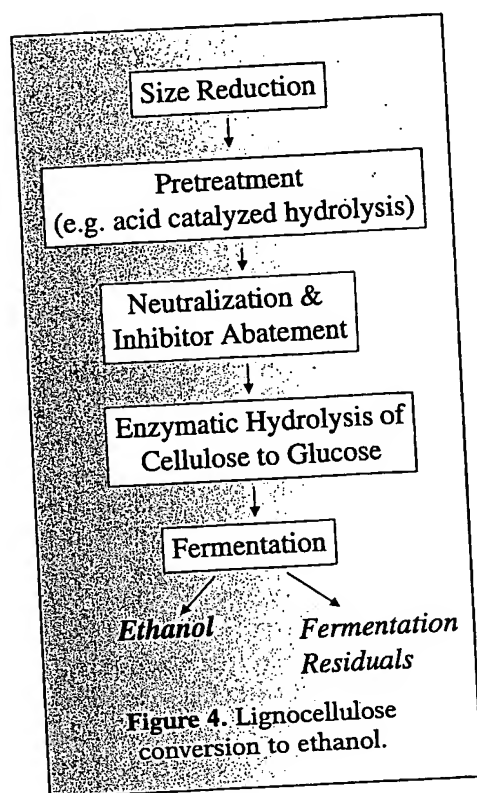
Modified milling processes have been demonstrated in the laboratory that allow for recovery of germ and pericarp fractions. By allowing the gluten to remain with the starch, steeping times can be greatly reduced and SO<sub>2</sub> eliminated (Singh and Eckhoff, 1996). The corn is soaked (31% solids loading) for 12 hr in 0.5% lactic acid at 59°C followed by milling to release the germ (Singh and Eckhoff, 1996). The germ is separated in a germ cyclone. Fiber is either recovered

with the germ by adjusting the density of the slurry through the cyclone or after germ collection by re-adjusting the slurry density and passing it through an additional cyclone (Wahjudi *et al.*, 2000). Removal of the germ and fiber allows for collection of corn oil and increased ethanol productivity (per bioreactor volume) because the fiber load is reduced from 18 to either 14 or 10% (dw/dw) (Taylor *et al.*, 2001). Capital costs for a 31 million gal ethanol/yr using the Quick Fiber process are forty-nine million U.S. dollars. A comparable dry grind plant is estimated to cost thirty-eight million dollars (Singh *et al.*, 2001). For crude corn oil selling at \$0.55/kg, an additional \$0.01 per litre can be realized in net additional income for the Quick Fiber vs. conventional dry grinding (Taylor *et al.*, 2001).

#### Lignocellulosic biomass conversion

Approximately 11% of the carbohydrates present in corn are not in the form of starch. These fractions consist of cellulose and xylan present in the hull (i.e., pericarp) and germ meal, and are folded in the corn gluten feed (wet milling) and DDGS (dry grinding). Removing part of the fiber from the feed co-products would increase their relative protein contents and, therefore, their value on a weight basis. These feedstocks are, also, conveniently located at ethanol plants. The amount of ethanol that could be produced is significant (Table 2). However, DDG contains considerable quantities of yeast, which might interfere with pretreating it for fermentation. Conversion to a modified dry grind mill would allow for collection of the fibrous fractions prior to starch fermentation. In addition to the fibrous component of the kernel, the rest of the corn plant (e.g., corn stover) could also serve as a feedstock for ethanol. Corn stover contains 58% carbohydrates (Table 2) and 1.0-1.5 lb of stover is produced per lb of harvested corn (Wiselogle *et al.*, 1996). Unlike DDG and corn fiber, collecting and storing corn stover represents a formidable





challenge. However, fermenting available corn stover could conceivably boost ethanol production 10 fold. There is a commercial corn stover collection facility in Harlan, IA (Glassner *et al.*, 1998).

A considerable amount of research has gone into developing processes for conversion of fibrous biomass into ethanol. A simplified schematic of what such a process would look like is shown as Figure 4. The first step is to prepare the biomass for fermentation by pre-treating. While size reduction will not be required for treatment of corn fiber, some type of milling will be needed for corn stover. A successful pretreatment step should accomplish multiple goals: (1) converting the xylan fractions to monosaccharides in high yields, (2) forming a minimum of inhibitors, and (3)

making the cellulose fraction susceptible to enzymatic hydrolysis by cellulase. Inhibitors are formed by subsequent degradation of sugars freed during hydrolysis, releasing organic acid side-groups (e.g., acetate) from the xylan component, and also from lignin break down products. Conditions that optimize cellulose recovery tend to also favor degradation of the xylan sugars and, therefore, optimal pretreatment conditions require a compromise. A wide variety of pretreatments have been investigated for biomass, and the best pretreatment, as expected, depends upon the source of biomass.

Most pretreatments are either chemical or a combination of chemical and physical (for review: Hsu T.A., 1996). Pretreatments described in the literature include: dilute acid, strong acid, alkaline hydrogen peroxide, ammonium fiber explosion (AFEX), steam explosion with  $\text{SO}_2$ , and hot water. Pretreating with acid is capable of completely hydrolyzing the xylan fraction. Alkali and hot water methods will only dissolve and partially hydrolyze xylan. This means hydrolysis will need to be completed using either enzymes or acid. Steam explosion tends to be more destructive to pentose sugars than some of the other methods. Acid pretreatments are the only ones that have been used commercially. For efficient recovery of the xylan sugars, the cellulose fraction needs to be hydrolyzed in a separate step.

Hydrolysis of the cellulose fraction, to release glucose, can be accomplished enzymatically or chemically. Acid hydrolysis, under sufficiently harsh conditions, can completely hydrolyze cellulose to glucose.

However, these harsh conditions lead to the formation of inhibitors and, so, (in the literature) enzymatic digestion has been favored. Often, the cellulase enzymes are added to the fermentation broth and carried out as a simultaneous saccharification and fermentation. Carrying out hydrolysis during the fermentation lowers the amount of enzyme required and circumvents the sensitivity of the cellulase enzymes to end product inhibition. Even when the best treatment for pre-treating cellulose is used, cellulase loading is much higher than that needed for amylases. Thus, the cost of cellulases is considered a major technical constraint to implementing biomass fermentations.

Corn fiber, corn bran, and corn germ meal are readily hydrolyzed with dilute acid (Asghari *et al.*, 1996, Dien *et al.*, 1999, Grohmann and Bothast, 1997, Saha and Bothast, 1999). Dilute sulfuric acid hydrolysis of corn fiber at 140-160°C and pH 1.5 - 2.0 for 10-30 min followed by enzymatic saccharification of dextrins gave a yield of 81-87% of total carbohydrates as free sugars (Grohmann and Bothast, 1997). Only 7 international filter paper units of cellulase per g corn fiber cellulose were required, which is 2-7 times less activity than usually added to dilute acid pretreated cellulose (ibid). Other pretreatments used with corn fiber (AFEX, alkaline peroxide, and hot water), while effectively preparing cellulose for enzymatic treatment, do not completely hydrolyze the xylan (Weil *et al.*, 1998, Moniruzzaman *et al.*, 1997, Leathers and Gupta, 1999). Hydrolysis of AFEX treated corn fiber xylan with commercial xylanases only converted 25% to monosaccharides (Hespell *et al.*, 1997). Corn germ xylan was more readily digested (ibid). The relative digestibility of hot water treated corn fiber xylan has not yet been reported. The AFEX hot water treatments are still of interest because they do not generate a large waste, which is associated with neutralization of the dilute-treated biomass, and have low concentrations of microinhibitors.

Table 3. Comparison of recombinant microorganisms for production of ethanol

Pretreatment	Strain	Max ethanol (g/litre)	Yield <sup>a</sup> (g/g)	Max. productivity (g/litre/hr)
Dilute acid	<i>E. coli</i> K011	34.7	0.41	1.16
Dilute acid	<i>E. coli</i> SL40	31.7	0.42	1.12
Dilute acid	<i>E. coli</i> FBR3	28.0	0.46	0.97
Dilute acid	<i>Zymomonas</i> CP4 (pZB5)	22.6	0.47	1.05
AFEX	<i>Saccharomyces</i> 1400 (pLNH32)	21.0	0.50	1.60

<sup>a</sup> Ethanol per grams sugar consumed; maximum possible is 0.51 g/g.

## What's on Your Mind?

### March on the Sugar Technology Forum

March on the Sugar Technology forum was much quieter than the first months of the year, perhaps members had exhausted themselves reading and writing! Just under 50 messages were posted and, as there are always topics being discussed, some topics were carried over from February.

There was no clear leader this month and no particular sector of the industry stood out although it was good to see at least two topics – alcohol production and cossette handling – which were quite focused. In general, many of the topics discussed are common to both beet and cane (the process house and beyond in particular) and hence are relevant to more members but this should not stop you from asking or commenting on subjects related to just one sector.


One of the ongoing topics was the question of molasses exhaustion. It is no wonder that such an important subject should receive attention, guiding less experienced members to improve their overall recoveries. Another of the topics from previous months was more of a flash-back as information which had been requested several weeks before if the topic was to be fully understood finally became available. The question related to flue gas energy losses up the stack, another important efficiency parameter which many people do not appreciate.

One of the key new questions earlier in March was the question of product sugar specification. It is clear that 'brown sugar' cannot really be specified and that 'white sugar' specifications vary around the world, usually with several different specifications covering different ranges of parameters applying for different uses.

Later in the month the question which stood out was how to split cossettes (the name given to the slices of beet prepared for extraction) between two extraction lines. The question came from a member faced with solving the problem for an expansion project and the assistance provided was both professional and prompt. We are looking forward to hearing of success in the future.

It is now almost a year since the forum was set up on Yahoo! and long-standing members will recall the reasons for doing so as the previous host staggered along. There is no doubt that the split left many people confused and, although necessary at the time, was not for the ultimate good of the industry and its technologists. We are therefore currently talking to see whether a merger cannot be achieved and hope to have more news soon.

If you want to know more then the forum web address is <[HTTP://GROUPS.YAHOO.COM/GROUP/SUGARTECH](http://groups.yahoo.com/group/SUGARTECH)> and you can join the forum at <[WWW.SUCROSE.COM/FORUM](http://WWW.SUCROSE.COM/FORUM)>

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Fermentation of the sugars recovered from the xylan fraction is problematic because the traditional yeast, *S. cerevisiae*, does not ferment pentoses. Naturally occurring yeast that do ferment xylose require aeration for growth, have low productivity, are acutely sensitive to inhibitors - especially acetate, and have fairly low ethanol tolerances. There are no commercially suitable naturally occurring bacteria or yeast for fermenting xylose to ethanol (Bothast *et al.*, 1999). Therefore, research has focused upon developing recombinant organisms to ferment pentoses to ethanol. Two strategies have been used to develop the needed biocatalyst: (1) expressing genes needed for xylose utilization in efficient ethanol producing microorganisms or (2) expressing genes needed for ethanol production in bacteria capable of using xylose and arabinose. As examples of the first approach, *Saccharomyces sp.* (Hahn-Hägerdal *et al.*, 2001; Ho *et al.*, 1998) and multiple *Zymomonas mobilis* strains (Zhang *et al.*, 1995) have been constructed that ferment xylose. Examples of the second approach are ethanologenic *E. coli* strains (Dien *et al.*, 1999, Ingram *et al.*, 1998, Ohta *et al.*, 1991). Several of these recombinant organisms have been used to ferment corn fiber hydrolysate (Table 3; Bothast *et al.*, 1999). Of those listed in Table 3, only the *K. oxytoca* and *E. coli* are capable of fermenting arabinose. Arabinan represents 3-5% of the total carbohydrates of corn stover (Wiselogle *et al.*, 1996) and 16% of that for corn fiber (Grohmann and Bothast, 1997).

A scalable process for converting corn fiber to ethanol has been demonstrated by the authors (Dien *et al.*, 1999). Specifically, the xylan portion was fermented, which left the cellulose fiber available for use in animal feed. The corn fiber was mixed with dilute acid (1.1 % v/v sulfuric acid) to form a 17% (dry wt/total wt) solids loading. The mixture was pumped into a reactor vessel equipped with an external jet siphon mixer and a steam jacket. The slurry entered the reactor through the jet siphon, which allows

fiber was held in the tank for 15 minutes at 145°C. The liquid portion was recovered for fermentation. The hydrolysate syrup contained a total of 76 g/litre of sugars, which is 95% of theoretical, excluding cellulose. The corn fiber hydrolysate was next overlimed to remove inhibitors. This process consists of adjusting the pH to 10 with  $\text{Ca}(\text{OH})_2$  and treating the hydrolysate to 90°C for 30 minutes. The hydrolysate was neutralized with sulfuric acid to pH 7 and the resulting gypsum formed removed by centrifugation. Yeast extract and tryptone were added as nitrogen sources. The hydrolysates were fermented using an ethanologenic *E. coli* strain. The fermentation was completed within approximately 65 hours and the ethanol yield was 92% of theoretical. Residual xylose was 3.5 g/litre.

Even if ethanol production is increased to 5 billion gallons per year by 2012, as being considered by the U.S. Congress, fuel ethanol would only displace 3.05% of the U.S. projected automotive fuel demand. Increasing ethanol supplies to greater production levels will eventually require fermenting lignocellulosic biomass (e.g. corn stover). Likewise, even though corn hulls and germ contain lignocellulose, they are also in limited supply as an ethanol feedstock. However, fermentation of these fibrous material can act as a stepping stone towards development of other, more challenging source so biomass, such as corn stover.

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### *La industria del etanol de maíz en los Estados Unidos: Una visión global de la tecnología actual y las perspectivas de futuro*

#### *Resumen*

El año pasado, se produjeron en los Estados Unidos, 1,77 billones de galones de etanol combustible, más del 90% del cual proviene del maíz. Se estima que la demanda de etanol llegará a más del doble en los próximos años ya que es utilizado para reemplazar el combustible oxigenado: metil ter-butil-eter (MTBE). Para la fermentación de etanol, el maíz se prepara ya sea por molienda húmeda o triturando a seco. La mayoría de las nuevas plantas de etanol utilizan molienda en seco ya que las inversiones de capital son más bajas. No obstante, los molineros de maíz en húmedo han expandido la producción agregando sobre plantas existentes. La tecnología actual da lugar a 2,5 (molienda húmeda) o 2,7 (molienda seca) galones de etanol por bushel de maíz. Es posible incrementar este rendimiento si los componentes fibrosos del grano de maíz (por ejemplo el pericarpio y germen) también son convertidos a etanol. La fermentación de estas fracciones no amiláceas podría aumentar el rendimiento de un bushel de maíz en un máximo de 10%. En esta reseña breve se exploran los aspectos técnicos y económicos de la producción de etanol, y también las perspectivas futuras para incrementar el rendimiento de etanol de maíz mediante la fermentación de las fracciones no amiláceas.

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# New Technologies in Ethanol Production

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# New Technologies in Ethanol Production

**C. Matthew Rendleman and Hosein Shapouri**

## Abstract

Fuel ethanol production has increased steadily in the United States since the 1980s, when it was given impetus by the need to reduce energy dependence on foreign supplies. The momentum has continued as production costs have fallen, and as the U.S. Clean Air Act has specified a percentage of renewable fuels to be mixed with gasoline. The fraction of annual U.S. corn production used to make ethanol rose from around 1 percent in 1980 to around 20 percent in 2006, and ethanol output rose from 175 million gallons to about 5.0 billion gallons over the same period. New technologies that may further increase cost savings include coproduct development, such as recovery of high-value food supplements, and cellulosic conversion. High oil prices may spur the risk-taking needed to develop cellulose-to-ethanol production. Developments such as dry fractionation technology, now commercially viable, may alter the structure of the industry by giving the cheaper dry-grind method an edge over wet milling. Dry milling requires smaller plants, and local farmer cooperatives could flourish as a result. Though improvements in processing and technology are important, however, the fluctuating price of inputs such as corn, the cost of energy alternatives, and environmental developments play larger roles in the fortunes of the industry.

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## Introduction

The use of ethanol for fuel was widespread in Europe and the United States until the early 1900s (Illinois Corn Growers' Association/Illinois Corn Marketing Board). Because it became more expensive to produce than petroleum-based fuel, especially after World War II, ethanol's potential was largely ignored until the Arab oil embargo of the 1970s. One response to the embargo was increased use of the fuel extender "gasohol" (or E-10), a mixture of one part ethanol made from corn mixed with nine parts gasoline. Because gasohol was made from a renewable farm product, it was seen in the United States as a way to reduce energy dependence on foreign suppliers.

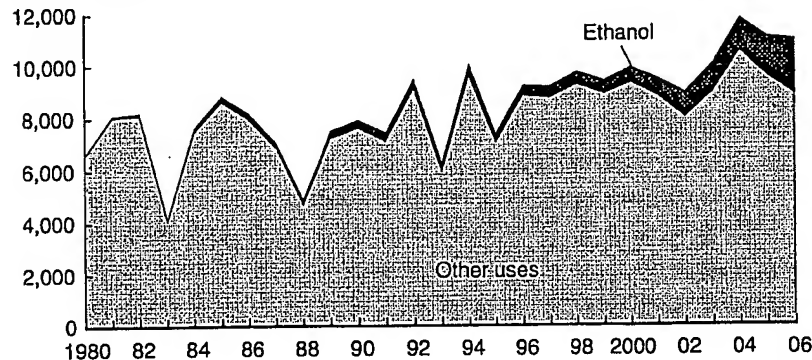
After the oil embargo ended, the use of ethanol increased, even though the price of oil fell and for years stayed low. Ethanol became cheaper to make as its production technology advanced. Agricultural technology also improved, and the price of corn dropped. By 1992, over 1 billion gallons of fuel ethanol were used annually in the United States, and by 2004 usage had risen to over 3.4 billion gallons. Many farm groups began to see ethanol as a way to maintain the price of corn and even to revitalize the rural economy. This economic support for ethanol coincided with a further justification for its use: to promote clean air. A 10-percent ethanol mixture burns cleaner than gasoline alone (reducing the emission of particulate matter, carbon monoxide, and other toxins), giving ethanol a place in the reformulated gasoline (RFG) market.

Ethanol use has also been boosted by the U.S. Clean Air Act and its various progressions. Originally, the Clean Air Act required wintertime use of oxygenated fuels in some urban areas to ensure more complete burning of petroleum fuels. Since ethanol contains 35 percent oxygen, this requirement of the act could be met by using an ethanol-containing blend. The current Energy Act eliminates the need for oxygenates per se in RFG, but it specifies the minimum amount of renewable fuels to be added to gasoline.

Figure 1

### Ethanol's use of U.S. corn production

Millions of bushels



Source: *Feed Situation and Outlook Yearbook*, USDA, Economic Research Service, various years.



By 1980, fuel ethanol production had increased from a few million gallons in the 1970s to 175 million gallons per year. During the 1990s, production increased to 1.47 billion gallons, and total production for 2006 is expected to be about 5.0 billion gallons. Annual U.S. plant capacity is now over 4.5 billion gallons, most of it currently in use. Demand is rising partly because a number of States have banned (or soon will ban) methyl tertiary-butyl ether (MTBE), and ethanol is taking over MTBE's role (Dien et al., April 2002). Ethanol provides a clean octane replacement for MTBE. The California Energy Commission and the California Department of Food and Agriculture now support ethanol development, and ethanol's use in California alone is expected to reach 1.25 billion gallons by 2012 (Ross).

The fraction of the Nation's annual corn production used to make ethanol rose from around 6.6 million bushels in the early 1980s (1 percent) to approximately 2 billion bushels in 2006 (20 percent) (fig. 1).

## Changes Since the 1993 ERS Analysis of Ethanol Production

In 1993, USDA's Economic Research Service (ERS) published *Emerging Technologies in Ethanol Production*, a report on the then-current state of ethanol production technology and efficiency (Hohmann and Rendleman). The report included a summary of production costs (table 1) and predictions of "near-term" and "long-term" technological advances that many believed would bring down ethanol costs.

The numbers were based on the costs of wet milling, which was then by far the greatest source of output. (Milling types are explained in the next section.) The estimate included a capital cost component, which distinguished this estimate from others done at the time. Other estimates ranged from \$1.08 to \$1.95 per gallon.

The near-term technologies listed in the ERS report were as follows:

- Gaseous injection of sulfur dioxide and the use of special corn hybrids,
- Membrane filtration,
- Other advances, including improved yeast strains and immobilization of yeast in gel substrates.

Long-term technologies (potentially available in 5 to 10 years) were as follows:

- Bacterial fermentation,
- Conversion of corn fiber to ethanol (cellulosic conversion),
- Coproduct development.

Though the savings from technological improvements are significant, they tend to be small compared with fluctuations in the net cost of corn, the main ethanol feedstock. This is illustrated in table 2, which presents data on corn costs and profits from the coproduct DDGS (distiller's dried grains with solubles) in dry-mill ethanol production from 1981-2004. Since 1981, sales of DDGS have recovered nearly half the cost of each bushel of corn used to produce ethanol, peaking in 1986, when over 66 percent of the feedstock cost was recovered this way. In recent years, the percentage of recovery has fallen because increased demand for ethanol has led to an abundance of DDGS, lowering its price on the feed market.

The near- and long-term technologies listed in the 1993 ERS analysis were predicted to save from 5 to 7 cents per gallon in the short term and from 9

Table 1  
**Ethanol wet-mill cost estimates, 1993**

Cost category	Cost per gallon
Feedstock	\$0.44
Capital	\$0.43
Operating	\$0.37
Total	\$1.24

Source: Hohmann and Rendleman (1993).

Table 2

**Net corn costs of dry milling, 1981-2004<sup>1</sup>**

Year	Corn value	DDGS* value	Byproduct value	Net corn cost	Net corn cost
	<i>\$/bu</i>	<i>\$/bu</i>	<i>% corn cost</i>	<i>\$/bu</i>	<i>\$/gal. ethanol</i>
1981	2.47	1.25	50.5	1.22	0.45
1982	2.55	1.21	47.5	1.34	0.50
1983	3.21	1.47	45.7	1.74	0.65
1984	2.63	0.83	31.6	1.80	0.67
1985	2.23	0.92	41.1	1.31	0.49
1986	1.50	1.00	66.4	0.50	0.19
1987	1.94	1.16	59.9	0.78	0.29
1988	2.54	1.20	47.2	1.34	0.50
1989	2.36	1.06	44.8	1.30	0.48
1990	2.28	1.08	47.3	1.20	0.45
1991	2.37	1.04	43.9	1.33	0.49
1992	2.07	1.04	50.4	1.03	0.38
1993	2.50	1.05	42.1	1.45	0.54
1994	2.26	0.91	40.1	1.35	0.50
1995	3.24	1.29	39.7	1.95	0.72
1996	2.71	1.21	44.8	1.50	0.55
1997	2.43	0.93	38.4	1.50	0.55
1998	1.94	0.72	37.2	1.22	0.45
1999	1.82	0.68	37.3	1.14	0.42
2000	1.85	0.69	37.0	1.16	0.43
2001	1.97	0.68	34.6	1.29	0.48
2002	2.32	0.75	32.3	1.57	0.58
2003	2.42	0.98	40.6	1.44	0.53
2004	2.06	0.65	31.3	1.41	0.52
Average	2.32	0.99	43.0	1.33	0.49

\*Distiller's dried grains with solubles.

<sup>1</sup>2.7 gal. of ethanol and 17 lbs of DDGS per bushel of corn.Source: ERS Feedgrains Database, <http://www.ers.usda.gov/db/feedgrains>.

to 15 cents by 2001. The savings have been as anticipated, but they have not come in the manner predicted.

Gaseous injection of sulfur dioxide was beginning in 1993 and is a part of the quick-germ (QG) and quick-fiber (QF) techniques currently being developed. There is revived interest in the use of special corn hybrids high in starch, though their use is still not widespread. Membrane filtration and yeast immobilization were being used in some plants in 1993, but their use, contrary to expectations, has not increased. Bacterial fermentation is still not used commercially, nor is cellulosic conversion of corn fiber. There have been no outstanding developments in coproducts, but the potential remains for their future exploitation. Most of the cost savings have been through plant automation and optimization of existing processes.

The industry is still improving technologically. It is far more mature than in 1993, and new developments appear poised to bring costs down further and to reduce the environmental impact of producing ethanol. In this report, we examine various production technologies, beginning with input improvements and then discussing process improvements, environmental technologies, and technologies involving coproducts. Finally, we look at niche markets and briefly examine cellulosic conversion.

## Ethanol's Energy Efficiency

Improvements in ethanol's energy consumption have continued since large-scale commercial production began in the 1970s. The process has become more efficient at using the starch in the corn kernel, approaching the theoretical limit of about 2.85 gallons of ethanol per bushel. Energy for conversion has fallen from as high as 70,000 Btu's per gallon in the late 1970s (Wang, August 1999) to 40,000 Btu's or less for modern dry mills and to 40,000-50,000 Btu's for wet mills. Modern energy-saving technology and process optimization account for the improvement.

In 2002, Shapouri et al. surveyed energy values and reported that fuel ethanol from corn produced about 34 percent more energy than it took to produce it. That figure was based on a weighted average of a 37-percent increase in energy from ethanol produced in dry mills and a 30-percent increase from wet mills. This value was revised in 2004 by updating energy estimates for corn production and yield, improving estimates of energy required to produce nitrogen fertilizer and energy estimates for seed corn, and using better methodologies for allocating energy for producing coproducts. With these revisions, the energy gain is 57 percent for wet milling and 77 percent for dry milling, yielding a new weighted average of 67 percent.

The energy content, however, may be less important than the energy replaced. A gallon of ethanol can save 26,575 Btu's of energy by replacing a gallon of gasoline because of ethanol's higher combustion efficiency (Levelton Engineering Ltd. and (S&T)2 Consulting Inc.). A gallon of ethanol containing 76,330 Btu's is able to replace a gallon of gasoline containing about 115,000 Btu's because ethanol's higher octane rating (113-115, compared with 87) allows high-compression engines to perform as well with fewer Btu's.

## Ethanol Production Processes

Though new technology may eventually blur the distinction between them, ethanol is produced by one of two processes: wet milling and dry milling. Wet mills are more expensive to build, are more versatile in terms of the products they can produce, yield slightly less ethanol per bushel, and have more valuable coproducts. Wet milling initially accounted for most of the ethanol fuel production in the United States, but new construction has shifted to dry mills, partly because dry mills cost less to build. In 2004, 75 percent of ethanol production came from dry mills and only 25 percent from wet mills (Renewable Fuels Association). As a result, most new technologies are being developed for dry-mill production.

Dry-milling plants have higher yields of ethanol; a new plant can produce 2.8 gallons per bushel, compared with about 2.7 gallons for wet mills. The wet mill is more versatile, though, because the starch stream, being nearly pure, can be converted into other products (for instance, high-fructose corn syrup (HFCS)). Coproduct output from the wet mill is also more valuable.

In each process, the corn is cleaned before it enters the mill. In the dry mill, the milling step consists of grinding the corn and adding water to form the mash. In the wet mill, milling and processing are more elaborate because the grain must be separated into its components. First, the corn is steeped in a solution of water and sulfur dioxide ( $\text{SO}_2$ ) to loosen the germ and hull fiber. This 30- to 40-hour extra soaking step requires additional tanks that contribute to the higher construction costs. Then the germ is removed from the kernel, and corn oil is extracted from the germ. The remaining germ meal is added to the hulls and fiber to form the corn gluten feed (CGF) stream. Gluten, a high-protein portion of the kernel, is also separated and becomes corn gluten meal (CGM), a high-value, high-protein (60 percent) animal feed. The corn oil, CGF, CGM, and other products that result from the production of ethanol are termed coproducts.

Unlike in dry milling, where the entire mash is fermented, in wet milling only the starch is fermented. The starch is then cooked, or liquefied, and an enzyme added to hydrolyze, or segment, the long starch chains. In dry milling, the mash, which still contains all the feed coproducts, is cooked and an enzyme added. In both systems a second enzyme is added to turn the starch into a simple sugar, glucose, in a process called saccharification. Saccharification in a wet mill may take up to 48 hours, though it usually requires less time, depending on the amount of enzyme used. In modern dry mills, saccharification has been combined with the fermentation step in a process called simultaneous saccharification and fermentation (SSF).

Glucose is then fermented into ethanol by yeast (the SSF step in most dry-milling facilities). The mash must be cooled to at least 95° F before the yeast is added. The yeast converts the glucose into ethanol, carbon dioxide ( $\text{CO}_2$ ), and small quantities of other organic compounds during the fermentation process. The yeast, which produces almost as much  $\text{CO}_2$  as ethanol, ceases fermenting when the concentration of alcohol is between 12 and 18 percent by volume, with the average being about 15 percent (Shapouri and Gallagher). An energy-consuming process, the distillation step, is required

to separate the ethanol from the alcohol-water solution. This two-part step consists of primary distillation and dehydration. Primary distillation yields ethanol that is up to 95-percent free of water. Dehydration brings the concentration of ethanol up to 99 percent. Finally, gasoline is added to the ethanol in a step called "denaturing," making it unfit for human consumption when it leaves the plant.

The coproducts from wet milling are corn oil and the animal feeds corn gluten feed (CGF) and corn gluten meal (CGM). Dry milling production leaves, in addition to ethanol, distiller's dried grains with solubles (DDGS). The feed coproducts must be concentrated in large evaporators and then dried. The CO<sub>2</sub> may or may not be captured and sold.

## **Input Improvements: Higher-Ethanol-Yielding Corn**

Efficient ethanol plants can convert 90-97 percent of the corn's starch content to ethanol. However, not all batches of corn leave the same amount of starch residue. Studies of ethanol yields from different batches show significant variability (Dien et al., March 2002). Even though it is the starch that is turned into ethanol, researchers have been unable to find a correlation between starch content (or even starch extractability) and the final yield of ethanol (Singh and Graeber). Researchers believe some starches are in a more available form (Dien et al., March 2002). They do not know, however, what makes the starch break down easily to simple sugars and why this trait varies from hybrid to hybrid (Bothast, quoted in Bryan, 2002). Some research shows that although the ease with which the starch breaks down varies among hybrids, most of the variability in the breakdown is due to other factors (Haefele et al.).

Seed companies like Pioneer, Monsanto, and Syngenta are working to create corn that will boost ethanol yield. "Current work centers on identifying highly fermentable hybrids we already have," says a Monsanto spokesman (Krohn). Pioneer reports yield increases of up to 6 percent in batches using what it calls HTF corn (High Total Fermentables), compared with the yields from unselected varieties (Haefele et al.). Monsanto calls its selected varieties HFC for High Fermentable Corn.

Syngenta Seeds' Gary Wietgreffe points out several of the impediments to widespread adoption of HTF corn (Ed Zdrojewski in *BioFuels Journal*, 2003b). To begin with, starch and ethanol yield vary by geographic region and from year to year, making an optimizing hybrid choice difficult. Further, choosing a hybrid that maximizes ethanol qualities may mean a tradeoff with yield and other potentially valuable qualities, such as protein content and even test weight (because of moisture). Testing equipment presents its own challenges. Not all units are calibrated the same, creating uncertainty. The technology may be less available to farmers than to ethanol plants, and even if it were to become more readily available, sorting grain by starch availability and making marketing decisions would be problematic for the grower. Finally, with ethanol plants already able to convert between 90 and 97 percent of the corn's starch, any new HTF or HFC genetics or technology would have to overcome the problems and significantly improve the profits of the ethanol plant and the farmer.

Higher ethanol yield leaves less DDGS for animal feed, possibly changing the quality as well as the quantity of the feed coproduct. A lower quantity might raise the protein percentage, but it could also concentrate some of the undesirable contents of the DDGS. Any changes, however, are expected to be minor. (See Haefele et al., p.14, on the selection of hybrids.)

Unlike many technologies that are adopted because they show an immediate improvement in profit or a reduction in risk, corn with a higher ethanol yield does not necessarily lead to additional profits for the farmer in today's marketing environment. Corn is not graded on the basis of fermentability, nor is a premium offered in the wider marketplace for this trait. In order to

overcome this market drawback, companies like Monsanto and Pioneer are developing programs to encourage the adoption of their selected hybrids.

So far, hybrid-testing research has centered on dry-mill production, the lower investment technique of choice for the new cooperatively owned plants. The seed companies are targeting their incentive programs on dry mills. Monsanto's program, "Fuel Your Profits," provides the participating ethanol plant with high-tech equipment that profiles the genetics of incoming corn and is calibrated to maximize ethanol yield (Rutherford). As an incentive, Monsanto gives rebates on E85 vehicles (those designed to run on 85%-ethanol fuel) and fueling stations. Pioneer has developed a whole-grain Near Infrared Test (NIT) to identify ethanol yield potential quickly.



## **Process Improvements**

New construction today is mostly of dry mills, and most new technology is designed for them. Major technology changes are made more efficiently while a plant is being built than when they are adopted later.

## **Advances in Separation Technologies**

New techniques that separate corn kernel components before processing will blur the distinction between wet and dry milling (dry grind) by allowing the dry mill to recover the coproducts from the germ. Process improvements are also being made that will reduce the cost of wet milling, generally by shortening the soaking step. Some of the separation improvements we describe here, though promising, are still experimental.

### ***Germ and Fiber Separation***

Modifications of the dry-grind facility have made the recovery of corn germ possible in dry milling. Normally, neither corn germ nor any other corn fraction is separated out before becoming part of the mash; all components go through fermentation and become part of the feed coproduct, DDGS. Various modifications of the process have made it possible to recover fiber and corn germ—and thus corn oil—from both the endosperm and the pericarp (outer covering) of the kernel.

A technique developed at the University of Illinois called Quick Germ (QG) allows recovery of corn oil and corn germ meal from the germ, making the dry mill a more profitable operation (Singh and Eckhoff, 1996, 1997; Taylor et al., 2001; Eckhoff, 2001). Results published in 1995 and 1996 demonstrated that with a 3- to 6-hour soak step (as opposed to 24 to 48 hours for the soak step in wet milling), the corn germ could be removed. Since then, research has explored the parameters of the process and its savings potential (Singh and Johnston). Another process, Quick Fiber (QF), can be used with QG to recover fiber from the pericarp, a source of potentially valuable food coproducts. Though these processes have not been used in commercial applications, they hold promise for reducing the net cost of the input corn. The tanks and equipment for the additional steps would increase the plant's capital cost, but could increase its capacity by reducing the amount of nonfermentables in the mash.

### ***Enzymatic Dry Milling***

This process, which uses newly developed enzymes, is another method with the potential for cost savings. In addition to recovering the germ and fiber from the pericarp, it allows recovery of endosperm fiber. Savings come from the recovered coproducts and from reduced energy consumption—the process requires less heat for liquefaction and saccharification. Plant capacity should be enhanced as well, since there is less nonfermentable material in the substrate because it is removed earlier in the process. The amount of DDGS is smaller, but of higher quality. Ethanol concentrations in

the mash are also higher. Industrial- and food-grade products can be recovered from the fiber. Alternatively, the fiber can be fermented.

### ***Dry Fractionation***

This recent technology separates the corn kernel into its components without the soaking step. Depending on the process—several companies currently offer similar technologies—the feedstock may be misted with water before being separated into bran, germ, and the high-starch endosperm portion of the kernel (*BioFuels Journal*, 2005d,e).

The advantages of dry fractionation over processes that require a soak step are threefold: lower costs because less energy is required for drying the feed coproduct, lower emissions, and greater coproduct output because the mash is more highly concentrated. The germ can be sold or pressed for corn oil, and the bran also has potential for food or energy use.

Dry fractionation is a process that has been tested and is in use in the food industry (Madlinger). Both new and planned ethanol plant construction employ the technology. Unlike some other new technologies, the dry fractionation equipment can be added to an existing dry mill.

With all the separation techniques, there appears to be less total ethanol recovered per bushel than with conventional dry-milling techniques, probably due to removal of some starch with the coproducts (Singh and Johnston). Each technique will change the nature of the resulting distiller's grains, potentially raising their value due to a higher protein content; the feed coproduct from the separation processes is purported to be higher in protein and lower in fiber than ordinary DDGS. However, research is needed to determine the feed value of this altered coproduct. Preliminary feed trials with poultry and hogs, as yet unpublished, are promising (Madlinger).

### ***Ammoniation Process in the Wet Mill***

Researchers have also investigated a separation technique involving pretreatment with ammonia (Taylor et al., 2003). This process would facilitate removal of the pericarp and reduce the soak time in wet milling or the QG process. Anhydrous ammonia would take the place of the caustic soda solution usually used in debranning. In laboratory research, the pericarp was more easily removed through ammoniation, but though the oil was not degraded, its quantity was reduced compared with conventional techniques.

### ***Continuous Membrane Reactor for Starch Hydrolysis***

This process, still experimental, uses enzymatic saccharification of liquefied corn in a membrane reactor. In a continuous membrane reactor, as opposed to the traditional batch process, starch would be broken down and glucose extracted continuously. Theoretically, the yield would increase, and the automated continuous process would enable better control than the batch process.

## ***Alkali Wet Milling***

In an experimental modification of the wet-milling process, corn was soaked briefly in sodium hydroxide (NaOH) and debranned (Eckhoff et al.). This process cut the costly soaking time to 1 hour. The pericarp removed in alkali wet milling becomes a potentially valuable part of the coproduct stream. Additional work is needed to develop ways of disposing of or recycling the NaOH before the technique can be commercialized.

## **New Ways of Fermentation**

### ***High-Gravity Fermentation***

This technique, still experimental, would lower water use in ethanol production. Potential savings would come from the reduced cost of water and wastewater cleanup, as well as from reduced energy use. This process would involve less heating and cooling per gallon of ethanol. Very-high-gravity fermentation accomplishes this saving in energy by using a highly concentrated mash with more than 30 percent solids. Experiments have resulted in a 23 percent-alcohol fermentation, much higher than with the conventional process. Commercial production at that level is not likely in the near future because of difficulty in staying within the required tolerances. However, incremental moves toward higher concentrations open the possibility of lower production costs.

### ***Improved Yeast***

For many years, researchers have been trying to improve yeast, which is a highly effective converter of sugars to ethanol. The desired end product is a yeast that would be more heat tolerant and better able to withstand high alcohol concentrations, that would produce fewer undesirable byproducts, and that might even be able to convert more types of sugar to ethanol. Developers have already made progress in some of these areas. For example, the ethanol tolerance of yeast is at least one-third higher today than in the 1970s.

Some researchers believe a yeast tolerant of temperatures as high as 140° F is the ideal. If such a yeast were to be developed—something increasingly possible with recombinant DNA techniques—the ethanol conversion process would look completely different than it does today (Novozymes and BBI International). Another goal of industry researchers is to produce less glycerol, which is produced in response to stress and represents a loss of ethanol during conversion.

### ***Conversion of Pentose Sugars to Ethanol***

Sucrose from starch is not the only type of sugar in the corn kernel. Some of the sugars are pentoses, or five-carbon sugars not normally utilized by common yeast. Any organism that could ferment pentoses to ethanol would be a valuable contribution to corn-ethanol conversion efficiency. This conversion has been achieved in the laboratory using genetically modified

yeasts (Moniruzzaman et al.) and in bacterial fermentation using *E. coli* (Dien et al., 1997). These processes are not in commercial use, partly because the engineered organisms are less hardy and less tolerant of environmental changes than conventional organisms. Researchers are also concerned about how the nutritional content of the resulting feed coproduct would differ from conventional DDGS and about whether the genetically modified organisms remaining in the feed would be acceptable in the commercial feed market.

## **New Enzymes**

### ***Enzymes for Liquefaction and Saccharification***

Enzymes were first used in ethanol production in the 1950s, but they have recently been improved and their cost brought down through the use of special fermentations of microorganisms. Costs have fallen 70 percent over the last 25 years (Novozymes and BBI International).

Enzymes enable chemical reactions to occur more easily, with less heat or a more moderate pH, and therefore more cost effectively. Their use in ethanol production improves liquefaction, saccharification, and fermentation. Enzyme use also results in reduced soak time, higher starch and gluten yield, better protein quality, and reduced water and energy use. USDA's Agricultural Research Service (ARS) is working with enzyme manufacturers to further reduce cost and improve effectiveness.

### ***Enzymes To Reduce Sulfur Dioxide and Steep Time in Wet Milling***

Part of the additional expense in wet milling as opposed to dry milling is the necessity of soaking the corn before separation of the germ from the kernel. The tanks increase capital cost, and the soak time slows the process. Soak time can be reduced by adding sulfur dioxide to the steep water, but research shows that the sulfur dioxide can be reduced or eliminated by using enzymes. Recently, an experimental two-stage procedure reduced soak time by up to 83 percent (Johnston and Singh; Singh and Johnston). In the saccharification step, the protease enzyme hydrolyzed the protein matrix around the starch granules and made it available for further breakdown. As with most enzymes, cost is still an issue; however, small-scale experiments seeking to optimize the process have so far reduced the enzyme requirement severalfold. Research trials show that using a low level of sulfur dioxide (more than 90 percent less than conventional levels) greatly reduces the enzyme requirement. Small amounts of sulfur dioxide are still effective in reducing bacterial contamination, a potential problem in continuous processes. Though enzymes are an added expense, the procedure has the potential to increase plant capacity (through the time savings), reduce energy costs, and allow the use of otherwise unusable broken grains. Replacing the conventional liquefaction and saccharification steps with a single, low-temperature enzyme step has already been discussed in the section "Advances in Separation Techniques."

## Distillation Technology

Standard distillation techniques leave about 4-percent water in the final ethanol. In the early days of ethanol distillation, the basic production design came from the beverage alcohol industry, where there is no need to remove all the water (Swain). Fuel ethanol, however, must be almost pure or dry, so ethanol producers began dehydrating their ethanol using a technique called azeotropic distillation. This technique requires use of an ingredient, usually benzene or cyclohexane, to break the azeotrope—the point after which distillation becomes ineffective. The adoption of molecular sieves allows the modern plant to use less power, reduce original capital outlay, and eliminate potential exposure of workers to dangerous chemicals.

Molecular sieves use materials with microscopic pore sizes large enough to allow a molecule of one size to get through while blocking another. For example, in ethanol dehydration the molecular sieves have a pore diameter that allows a water molecule to enter and be trapped but keeps out the larger ethanol molecule. Since the late 1980s, vapor-phase molecular sieves have been the industry standard, improving on the liquid-phase sieves by reducing the required size (Novozymes and BBI International).

## Control Systems

The 1993 prediction of cost reductions in ethanol production (Hohmann and Rendleman) overlooked the incremental changes in efficiency that were taking place due simply to increased control of fermentation and other processes. Distributed control systems were already being used, but with the evolution of technology, especially computing capabilities, these systems have continued to reduce costs while optimizing the production process.

Distributed control systems are used in industrial and other engineering applications to monitor and control a process remotely. Human operators manage equipment distributed throughout the plant (or other application). Examples, besides ethanol plants, include power distribution systems, traffic signals, water management systems, and biorefineries. Instruments to measure and control, usually digital, are wired ultimately to computers, allowing a human-to-machine interface.

Merging the distributed control system with computer programs allows timely monitoring of processes, and even allows prediction. Reports can be compiled from stored data, and alarms can be set to alert operators if established parameters are breached.

Distributed control systems have cut costs in ethanol plants mainly by reducing the labor required, but they have also improved production efficiency in other ways, letting operators fine-tune processes they could not control as closely in the past. Better process control also reduces downtime and maintenance.

## Environmental Technologies

In addition to reducing the amount of energy required for production, modern ethanol plants give off fewer odors and emissions than ever before. Technological advances hold promise for converting more of the feed coproducts into ethanol, for reducing components of DDGS that might harm the environment, and for utilizing waste streams from the process.

As noted, modern ethanol production uses less energy as techniques and technologies improve. Both wet and dry millers are using less fuel and electricity per gallon produced, and farmers are producing corn more efficiently. All these savings are an environmental plus for ethanol.

Ethanol plant emissions are a second area of improvement. In 2002, Minnesota producers signed an agreement with the Environmental Protection Agency (EPA) to reduce emissions coming from their plants. That agreement has become an industry standard. Since then, ethanol producers in several States have agreed to install thermal oxidizers or other technologies that eliminate nearly all volatile organic compounds (VOCs) and other pollutants, adding equipment that averages more than \$2 million per plant. The EPA estimates that the agreement will eliminate more than 63,000 tons of pollution annually.

Though pollutants, like particulate matter and even VOCs, can originate from fermentation and from other parts of the plant such as grain-handling areas, most of the attention has been focused on dryer stacks. Thermal oxidizers are now standard equipment in most new ethanol facilities. They convert carbon- and hydrogen-bearing compounds into CO<sub>2</sub> and water through high-temperature oxidization. Besides eliminating odors and visible emissions, thermal oxidizers can eliminate over 99 percent of oxides of nitrogen and other hazardous air pollutants, as well as certain particulates.

Wastewater emission problems have been largely solved by the development of anaerobic digester systems. Majumdar et al. report using membrane technology to recover VOCs such as hexane from process air emissions, giving membranes a role in environmental remediation.

New techniques may make processing itself more environmentally friendly. For example, a corn-steeping process being developed by scientists from ARS and the University of Illinois uses enzymes and reduces the need for sulfites.

Another discovery—one that may hold the most promise for the future—is the conversion of low-value and waste stream products into valuable coproducts. (This will be discussed in the next section, "Technologies Involving Coproducts.")

Finally, overfeeding phosphorus to animals can be an environmental concern because the phosphorus ends up on the land as manure. The phosphorus available in DDGS is more than is needed for proper animal nutrition. If the level excreted over time is excessive, phosphorus can move into ground or surface water and create problems such as algae in the waterways. Researchers are experimenting with membrane technology that would remove phosphorus from the thin stillage (the liquid remaining after removal of the wet distiller's grains) before it becomes feed. The result is likely to be more efficient feed rations and reduced environmental impact.

## Technologies Involving Coproducts

In addition to animal feeds, other potential coproducts are produced along with the ethanol. Both wet and dry milling create CO<sub>2</sub> during fermentation. Minor components, such as glycerol, may be collected from the processing stream. Some research directions may alter the entire process, using different fermentations to produce entirely different product lines. Researchers are also hoping to turn much of the nonfuel product into ethanol, or even something more valuable than the fuel that is currently the primary product. Possibilities include protein and fiber that could be added to human foods to increase nutritional value.

Enzymatic milling may also allow recovery of valuable coproducts. Conventional dry milling leaves as coproducts distiller's dried grains with solubles and, if recovered, CO<sub>2</sub>. ARS scientists from USDA's Agricultural Research Service are adapting the concept of enzymatic milling to the dry-mill ethanol process, partly to recover additional high-value coproducts.

## The Growing Supply of Feed Coproducts

Ethanol production does not exhaust the feed value of corn; it merely uses up the starch portion, leaving protein, minerals, fat, and fiber to be dried and sold for feed. A high percentage of ethanol producers' revenue comes from the feed coproduct. Dry milling turns a bushel of corn (56 lb) into 2.7 or more gallons of ethanol and leaves 17 lb of distiller's grains. Wet milling produces only slightly less ethanol and coproduces around 16 lb of corn gluten meal (CGM, 2.65 lb) and corn gluten feed (CGF, 13.5 lb), in addition to corn oil. In 2004, 7.3 million metric tons of DDGS, 426,400 metric tons of CGM, and 2.36 million metric tons of CGF were produced (Renewable Fuels Association). Predictions for near-term increases are as high as 10 million tons by 2007-08, which would constitute a significant portion of all the cattlefeed in the United States (*BioFuels Journal*, 2005c).

Because feed coproducts and ethanol are produced in fixed proportions, increased demand for ethanol will result in greater output of DDGS, putting downward pressure on its price. Partly for this reason, research is continuing on alternative coproducts.

Proving the nutritional value of DDGS for new uses will expand the market. Most of the DDGS produced is fed to dairy and beef cows, but it is increasingly being tested and used in swine and poultry rations. Research is planned on DDGS in equine diets.

The nonuniform character of DDGS makes it difficult to establish feeding parameters because the product varies in consistency and nutritional value. Ongoing research is aimed at establishing feed values for various forms of DDGS, and some producers are developing proprietary DDGS brands with guaranteed nutritional properties.

## Sequential Extraction

Lawrence Johnson of Iowa State University has initiated several projects exploring the parameters of the sequential extraction process, or SEP (see, for example, Hojilla-Evangelista and Johnson). SEP uses alcohol rather than water to separate kernel components in an otherwise wet-mill process. The researchers claim increased ethanol production (10 percent), higher quality protein extracts (with no SO<sub>2</sub> needed for extraction, and therefore less degradation of the protein portion), and the production of corn fiber gum, a gum arabic substitute, as a coproduct. Gum arabic is used in producing soft drinks, candy, and pharmaceuticals. Cost remains a problem with the SEP process: The initial capital outlay for an SEP plant would be much higher than for a conventional wet mill. Extraction of proteins from the separated germ remains a problem as well.

## Corn Germ Recovery for the Dry-Mill Process

As explained in the "Process Improvements" section, both dry fractionation and the quick-germ technique modify the dry-mill process and make the recovery of corn germ possible. Recovery of the germ, and thus of the oil, can make dry milling more profitable. The soak step in the quick-germ process takes less time than in wet milling, 3-6 hours as opposed to 24-48 hours. The process has not yet been used commercially. Plants using dry fractionation, however, are underway. Profitability will depend on the relative cost of corn oil and the capital costs of the additional equipment required.

## Centrifugal Corn Oil Separation from the Distiller's Grain Stream

An additional technology for separating corn oil from distiller's grain has recently become available to dry millers. SunSource, a coalition of ethanol producers and a technology company, is licensing a system that can be installed in new plants or retrofitted to existing ones (Walker). The technology makes an additional coproduct available to ethanol producers, most likely to be used in biodiesel production. The process uses centrifuge technology to extract the oil from the distiller's grains in the evaporation step. The developers of the process claim that removing the oil from the distiller's grains does not lower the value of the feed coproduct and makes it easier to handle. The process also reduces volatile organic compounds emitted from the dryers, an environmental bonus.

## CO<sub>2</sub> Recovery

Ethanol's most abundant coproduct is CO<sub>2</sub>, produced by yeast in about the same proportion as ethanol itself. Only about 25 U.S. plants find uses for the gas (Lynn Grooms in *BioFuels Journal*, 2005b); the other plants, because of the low commercial value of CO<sub>2</sub>, simply vent it into the air. Most CO<sub>2</sub> sold commercially is used in soft drinks and food processing, while other uses, such as water treatment, welding, chemical processing, refrigerants, and hydroponics, consume some of the remainder.



Another approach would be to find new uses for the gas, raising its value and expanding the market. One experiment uses CO<sub>2</sub> to enhance the recovery of oil from depleted oilfields. The gas is pumped into the oil production zones, forcing residual oil to the surface. If successful, the technique could greatly expand the market for CO<sub>2</sub>.

A number of experiments with CO<sub>2</sub> are taking place at the basic science level (Bothast). One idea, successful at that level, is to turn the gas into ethanol or other fuel. However, the techniques are not yet commercially viable.

Bioconversion offers hope for increased CO<sub>2</sub> exploitation. Through biological processes, it turns organic materials into usable products or energy. In corn ethanol production, the possibility of bacterial bioconversion of CO<sub>2</sub> into fuel (e.g., ethanol or methanol) is under study.

### **Stillage Clarification and Other Uses of Membranes**

Membrane separation is now used in dry mills to treat incoming boiler water and in wet mills to clarify dextrose. Based on the molecular size of the particles permitted to pass through, membranes are classified as reverse osmosis, nanofiltration, ultrafiltration, or microfiltration. They are made of various materials, including organic polymer, ceramics, and stainless steel.

Membranes were once thought promising for removing the last of the water from ethanol—the portion left by ordinary distillation—as processors looked for substitutes for hazardous materials like benzene that were then used for that purpose. In plants built today, however, the drying part of ethanol production is done with molecular sieves.

Membrane systems are used in industry to separate, clarify, and concentrate various feed streams and are most efficient when used on dilute broths. In the future, they may be used to reduce the cost of production through recovering and purifying minor components of the ethanol product stream. The recovery of lactic acid and glycerol from thin stillage is an application of this research that may soon be commercially viable. Corn oil and zein, a protein, are also potentially recoverable (Kwiatkowski and Cheryan). Researchers think membranes can be useful in continuous (though not in batch) reactors (Escobar et al.).

### **Biorefinery**

One definition for a biorefinery is “a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass.” The concept is a bit like wet milling, but with more coproduct possibilities. Corn or another feedstock might be decomposed and recombined into a number of products other than, or in addition to, ethanol. Some of the products might be high-value, low-volume ones, outside the traditional ethanol market, that could supplement a plant’s primary, lower value product line.

## Extraction of Compounds from DDGS

The biorefinery concept meshes with a new area of research known as functional foods or nutraceuticals. Two categories of functional foods, dietary fibers and oligosaccharides, can be derived from grains.

Several Canadian companies and some universities are experimenting with extracting new coproducts from the distiller's grains generated from alternative feedstocks. Examples include cosmetics from oat derivatives, phenolic avenanthramides (useful in low-density lipoprotein resistance to oxidation) from oats and wheat, and beta-glucan, a fiber-type complex sugar derived from yeast, oats, and barley fiber and useful in reducing cholesterol.

A biorefinery may also yield purified proteins used as human food or in industrial processes. A potentially recoverable coproduct is zein, a corn protein that can be used in adhesives and in coatings for pharmaceuticals and packaging materials because of its good water-vapor barrier properties. ARS scientists are working to develop a cost-effective way to recover zein from the milling stream, potentially making its use more common.

## Corn Fiber Oil Recovery

Corn fiber is a byproduct of corn wet milling and may be a future product of dry milling. ARS has been developing methods to obtain enriched protein, starch, and fat from corn fiber. Corn fiber is also a source of corn fiber oil, a valuable dietary supplement that contains high levels of cholesterol-lowering and antioxidant phytosterols. Corn fiber can also be recovered by other means, such as the quick-fiber technique. Its economical recovery could give ethanol production another valuable coproduct line.

## Regional Impacts of Ethanol Plants

Ethanol production holds promise for rural communities that hope to add value to locally produced corn. A new ethanol plant is seen as a way to create jobs and revitalize the local rural economy. Such scenarios seem more likely with widely dispersed, smaller scale plants—the kind that could spring up to service small specialty markets with an unusual coproduct or to take advantage of a local feedstock or other regional characteristic.

In the future, corn-processing facilities may be able to recover special healthful elements. One example might be proteins recovered from the process stream by ultrafiltration and made available as food.

Minor producers may take advantage of discard items like soft drinks or candy past their expiration date or other unusual sources of feedstock. Two cheese plants in California produce ethanol and at the same time solve a disposal problem by using the whey—generally regarded as waste—as a feedstock. Cheese whey contains lactose that, if not fermented, may require special processing at the cheese plant to avoid extra charges for municipal water-disposal treatment.

Some ethanol producers take advantage of their location to reduce production costs by selling coproducts otherwise too bulky to transport, such as steep-water. Or they save by avoiding drying, for instance, by feeding their wet distiller's grains to cattle or even fish. Others may sell CO<sub>2</sub>, or may at least capture some value from it by using it in greenhouses to boost plant growth.

With the development of commercial cellulosic techniques, ethanol producers may actually be paid to take away material that they can use for feedstock—for instance, waste from other production systems or even municipal garbage.

Other potential niche markets may use animal waste. One current USDA research project seeks to exploit the advantages of co-location (of an ethanol plant and poultry farms) by generating electric power and steam for ethanol production from chicken litter. Coproduction of power and steam from a waste stream is being developed in another USDA project.

Many ethanol facilities recently opened or under construction are farmer owned and dispersed across rural areas. Farmers expect the completion of an ethanol plant in the area to increase the local corn price. McNew and Griffith examined the impact on local corn prices of opening 12 ethanol plants and found that, on average, price per bushel rose 12.5 cents at the plant and that some price response was detected 68 miles from the plant.<sup>1</sup>

New rural ethanol plants also provide employment. Though the plants need fewer employees than they would have just a few years ago when the industry was using less labor-saving technology, the U.S. Department of Energy (DOE) estimates that ethanol production is responsible for 40,000 jobs and \$1.3 billion in increased annual household income.

<sup>1</sup>McNew and Griffith have also established a Web site at Montana State University that shows how corn prices are impacted by the opening of an ethanol plant (*BioFuels Journal*, 2003a). The site allows the user to investigate a small, medium, or large plant and displays the results graphically in map format. The impacts are based on econometric work by the authors. The tool, called the "Ethanol Plant Analyzer: A GIS-Driven Tool for Assessing Ethanol Feasibility," can be found at <http://extensionecon.msu.montana.edu/eplantanalyzer/>

## National Benefits from Ethanol

Ethanol produced in the United States displaces imported foreign oil and creates domestic economic activity. Gallagher et al. (2000) estimate that the current program results in a \$400-million net gain in overall social welfare. More domestic production, which is likely with an MTBE phaseout, would result in additional gain.

With ethanol production of 3.41 billion gallons in 2004, 143.3 million fewer barrels of oil were needed, about 4.5 percent of annual U.S. use (Urbanchuk). A 10-percent mixture of E-10 reduces petroleum use by 6 percent, greenhouse gas emissions by 1 percent, and fossil energy use by 3 percent (Wang et al.).

Increased biomass production would also change the picture. Gallagher and Johnson focus primarily on the benefits of a developed biomass-to-ethanol industry. Assuming an industry based on corn stover, the largest single source of biomass, they conclude that U.S. welfare would increase (a) because of the expanded fuel supply and (b) because the oligopoly effects of pricing by the Organization of Petroleum Exporting Countries (OPEC) would be mitigated. A biomass-to-ethanol industry, based on something like switchgrass, could add to farmers' product line and "could significantly increase profits for the agricultural sector" (De La Torre Ugarte et al.).

## Biomass: Ethanol's Future?

Though corn has been the feedstock of choice in the United States, ethanol potentially can be made from any starch, sugar, or cellulosic feedstock. In fact, ethanol has been created from a variety of grains and from grass and straw, wood fibers, and sugarcane. Though ethanol production from corn has become more efficient, some experts see it as a technology that has already matured, with any significant reduction in production costs unlikely (DiPardo). Substantial cost reductions may be possible, experts believe, if cellulose-based feedstocks are used instead of corn. One industry publication editorializes: "Ultimately, if renewable automotive fuel becomes economical in the United States it will have to be made from lignocellulosic biomass" (*Industrial Bioprocessing*).

In the end, biomass-to-ethanol production may be attractive because biomass would cost less than corn. In addition, selling the feed coproducts from corn ethanol may become burdensome. As corn ethanol production increases, an inevitable result of dry-mill expansions, more feed coproducts will find their way into the market and drive down prices for DDGS.

The vision of cellulosic conversion is not yet commercial reality, however, due to difficulties inherent in turning biomass into ethanol. Because the cellulose and fermentable portions of woody biomass are tightly bound together, researchers have had to focus on the problem of pretreatment and hydrolysis. The necessary chemical conversion can take place using acids or enzymes, but, to be commercially viable, costs must be brought down. USDA and the U.S. Department of Energy are funding projects that have this aim. Also, many of the sugars making up cellulosic feedstocks (composed of cellulose and hemicellulose) are not readily convertible to ethanol by ordinary yeast.

Researchers have not settled on the cost of producing ethanol from biomass because ethanol is not yet being produced this way. A joint project by the USDA and DOE estimated the unit cost at a 25-million-gallon per year (MMgy) plant to be \$1.50 per gallon (1999 dollars) (McAloon et al.). Though some researchers put this figure lower, at \$1.16-\$1.44 per gallon (Wooley et al.), recent estimates of the cost of commercial cellulose collection (\$40-\$50 per ton) and capital outlays (over \$6 per gallon of annual capacity) make the likely cost higher. A consideration for new facilities will be the one-of-a-kind expense associated with setting up the first working biomass-to-ethanol plants (e.g., scaleup and development costs). In its \$1.50-per-gallon estimate, the USDA/DOE study assumed these costs had already been incurred.

## Cellulose to Ethanol: The Process

In the same way that starch from corn must be hydrolyzed and saccharified (decomposed further into simple sugars) before it can be fermented, cellulose must first be converted to sugars before it is fermented and turned into ethanol. Cellulosic feedstocks are more difficult than corn to convert to sugar. Cellulose can be converted by dilute acid hydrolysis or concentrated acid hydrolysis, both of which use sulfuric acid. Hydrolysis can also be

achieved with enzymes or by other new techniques, including countercurrent hydrolysis or gassification fermentation.

Cellulosic hydrolysis produces glucose and other six-carbon sugars (hexoses) from the cellulose and five-carbon sugars (pentoses) from hemicellulose. The non-glucose (carbon) sugars must be fermented to produce ethanol, but are not readily fermentable by *Saccharomyces cerevisia*, a naturally occurring yeast. However, they can be converted to ethanol by genetically engineered yeasts, though the process is not yet economically viable (DiPardo).

## Supplying Biomass

Some research has centered on converting the cellulosic portion of the corn kernel. Many of the researchers in this effort initially believed that cellulosic conversion could begin with the cellulose in the current feedstock stream (corn) and proceed to corn husks, and then to corn stover, before they finally extended their research to include other sources of cellulose. A second line of research has centered on converting cellulosic biomass directly into ethanol from noncorn sources such as small-diameter trees and switchgrass. Further research has focused on converting cellulose after it has entered the waste or coproduct stream, through steam explosion, for example.

If converting biomass to ethanol can be made economically attractive, the potential feedstocks are myriad. They include agricultural waste, municipal solid waste, food processing waste, and woody biomass from small-diameter trees. Agronomic research is underway on improving dedicated-energy crops such as hybrid willow, hybrid poplar, and switchgrass (DiPardo). One project looks at genetic improvement of switchgrass to optimize its conversion. Grasses grow quickly, of course, while tree crops such as willow require a 22-year rotation, with the first harvest in year 4 and subsequent harvests every 3 years thereafter. Hybrid poplar trees require 6-10 years to reach their first harvest.

Biomass from crop residue can be a source of farm profits, and with appropriate steps, its use in ethanol conversion can be environmentally friendly. A USDA study by Gallagher et al. (2003) concluded that crop residues are the cheapest prospective source of fuel for the U.S. market, with the energy potential to displace 12.5 percent of petroleum imports or 5 percent of electricity consumption.

## Biomass Byproducts: Problems with Acid and High Temperatures

The dilute acid and concentrated acid hydrolysis used in biomass-to-ethanol conversion produce byproducts that either must be disposed of or that require recycling of sulfuric acid. In addition, the high temperatures required take a toll on the sugars and thus on the ethanol yield (DiPardo).



## **Potential Solutions to Acid and Heat Problems**

**Countercurrent Hydrolysis**—Advances in biotechnology could reduce conversion costs substantially. The National Renewable Energy Laboratory (NREL) presents countercurrent hydrolysis as a new pretreatment. The process uses steam to hydrolyze most of the hemicellulose. In a second, hotter, stage, dilute sulfuric acid hydrolyzes the rest of the hemicellulose and most of the cellulose. NREL researchers believe the countercurrent hydrolysis process offers more potential for reducing costs than the dilute sulfuric acid process. They estimate that it will increase glucose yields and permit a higher fermentation temperature, resulting in an increased yield of ethanol. They have achieved glucose yields of over 90 percent in experiments with hardwoods (NREL, 2004).

**A New Approach**—While acknowledging that a cellulose-to-ethanol industry is in its infancy, Tembo et al. attempt to determine parameters that would define a regional (Oklahoma) biorefinery industry. The authors assess alternatives for future production, positing a gassification-fermentation technique that uses neither traditional acid nor enzymatic hydrolysis. Lignocellulosic biomass can be gassified, they say, in fluidized beds to produce "synthesis gas." The gas can then be converted by anaerobic bacteria to ethanol. Advantages to such a lignocellulosic system include a theoretically lower cost than for corn ethanol and the potential to use multiple perennial feedstocks, with supposedly less environmental impact than corn use. The researchers caution that the process is at the bench level and is not yet commercially available.

**Enzymatic Hydrolysis**—NREL believes that the greatest potential for ethanol production from biomass lies in enzymatic hydrolysis of cellulose. Advances in biotechnology may eventually make the technique possible through the use of genetically engineered bacteria and may also permit the fermentation of the pentoses.

## **Reducing Enzyme Costs**

The use of enzymes in biomass-to-ethanol conversion will require reductions in the cost of producing cellulase enzymes, along with an increased yield in the conversion of nonglucose sugars to ethanol. The enzyme cellulase, already used in industry, replaces sulfuric acid in the hydrolysis step. Higher sugar yields are possible because the cellulase can be used at lower temperatures (Cooper). NREL reports that recent process improvements allow simultaneous saccharification and fermentation, with cellulase and fermenting yeasts working together so that sugars are fermented as they are produced. NREL estimates that cost reductions could be four times greater for the enzyme process than for the concentrated acid process and three times greater than for the dilute acid process.

In speaking of both corn stover and forest product waste, *Industrial Bioprocessing* writes, "The big stumbling block in manufacturing ethanol from biomass is the cost of hydrolyzing cellulose into fermentable sugar." To speed the quest for cheaper ways of using enzymes to convert biomass to ethanol, DOE funded research by two commercial enzyme companies,

Novozymes and Genencor International Inc. Cellulase enzymes were recently reported to cost 45 cents per gallon of finished ethanol, making them too expensive for commercial use (NREL, 1998). NREL estimated that the cost could be reduced to less than 10 cents with scaled-up production. In fact, Novozyme recently announced that its researchers have successfully completed this project and have reduced the enzyme costs to 10-18 cents per gallon of ethanol produced (Susan Reidy in *BioFuels Journal*, 2005a).

### **Other Biomass-to-Ethanol Improvements**

NREL estimates that, in addition to reduced costs of enzyme conversion, improvements in acid recovery and sugar yield for the concentrated acid process could save 4 cents per gallon and that process improvements for the dilute acid technology could save about 19 cents per gallon.

Considerable success in cellulosic conversion has already been achieved at the experimental level. Depending on the prices of alternatives and the success of current scaleup efforts, commercial viability may be possible in the near term. A Canadian firm, Iogen Corporation, in partnership with the Canadian Government, has demonstrated a process that turns wheat straw into fermentable sugar.

## Conclusions: Ethanol's Potential

In keeping with USDA's early estimates of the savings to come, the cost of ethanol production has indeed fallen. Though improvements in process optimization and technology have been important, the fluctuating prices of inputs such as corn, the price of energy alternatives, and even environmental developments such as a drop in MTBE use, play larger roles in the fortunes of the industry.

Ethanol production is becoming a mature industry, with savings in the next 10 years likely to be smaller than those of the last 10-15 years.

Some developments, such as dry fractionation technology—soon to be commercially employed—may alter the structure of the industry by giving an edge to the less capital-intensive dry-mill method. This advantage for dry milling may make it easier to build smaller plants that are cost competitive, and local farmer cooperatives could flourish as a result.

Promising areas to be exploited by new technology include coproduct development, cellulosic conversion, and niche markets. The recovery of high-value food supplements may reduce financial risk by giving the industry an outlet outside the capricious energy market. Continued high oil prices may spur the risk-taking necessary to overcome the initial scaleup and development costs of cellulose-to-ethanol production. Niche markets that take advantage of locally available feedstocks, that have local outlets for coproducts, or that produce unique coproducts may also contribute to the industry's growth.

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U.S. Department of Energy Office of Science

# Genomics:GTL

## Systems Biology for Energy and Environment

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## Fuel Ethanol Production

How  
is

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### ethanol currently produced from corn?

In the United States, ethanol is produced primarily from starch in corn kernels. Most of the 4 billion gallons of ethanol produced in 2005 came from 13% of the U.S. corn crop (1.43 billion bushels of corn grain). When corn is harvested, the kernels make up about half of the above-ground biomass, and corn stover (e.g., stalks, leaves, cobs, husks) makes up the other half.

Ethanol production from corn grain involves one of two different processes: Wet milling or dry milling. In wet milling, the corn is soaked in water or dilute acid to separate the grain into its component parts (e.g., starch, protein, germ, oil, kernel fibers) before converting the starch to sugars that are then fermented to ethanol. In dry milling, the kernels are ground into a fine powder and processed without fractionating the grain into its component parts. Most

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ethanol comes from dry milling. Key steps in the dry mill ethanol-production process include:

1. **Milling.** Corn kernels are ground into a fine powder called "meal."
2. **Liquefying and Heating the Cornmeal.** Liquid is added to the meal to produce a mash, and the temperature is increased to get the starch into a liquid solution and remove bacteria present in the mash.
3. **Enzyme Hydrolysis.** Enzymes are added to break down the long carbohydrate chains making up starch into short chains of glucose (a simple 6-carbon sugar) and eventually to individual glucose molecules.
4. **Yeast Fermentation.** The hydrolyzed mash is transferred to a fermentation tank where microbes (yeast) are added to convert glucose to ethanol and carbon dioxide ( $\text{CO}_2$ ). Large quantities of  $\text{CO}_2$  generated during fermentation are collected with a  $\text{CO}_2$  scrubber, compressed, and marketed to other industries (e.g., carbonating beverages, making dry ice).
5. **Distillation.** The broth or "beer" produced in the fermentation step is a dilute (10 to 12%) ethanol solution containing solids from the mash and yeast cells. The beer is pumped through many columns in the distillation chamber to remove ethanol from the solids and water. After distillation, the ethanol is about 96% pure. The solids are pumped out of the bottom of the tank and processed into protein-rich coproducts used in livestock feed.
6. **Dehydration.** The small amount of water in the distilled ethanol is removed using molecular sieves. A molecular sieve contains a series of small beads that absorb all remaining water. Ethanol molecules are too large to enter the sieve, so the dehydration step produces pure ethanol (200 proof). Prior to shipping the ethanol to gasoline distribution hubs for blending, a small amount of gasoline (~5%) is added to denature the ethanol making it undrinkable.

## How is ethanol produced from cellulosic biomass?

Conversion of cellulosic biomass to ethanol is less productive and more expensive than the conversion of corn grain to ethanol. Cellulosic biomass, however, is a less expensive and more abundant feedstock than corn grain; more efficient processing is needed to take advantage of this plentiful and renewable resource. The structural complexity of cellulosic biomass is what makes this feedstock such a challenge to break down into simple sugars that can be converted to ethanol.

Most plant matter consists of three key polymers: Cellulose (35 to 50%), hemicellulose (20 to 35%), and lignin (10 to 25%). These polymers are assembled into a complex, interconnected matrix within plant cell walls. See [Understanding Biomass: Plant Cell Walls](#) for an illustrated description of plant cell-wall structure. Cellulose and hemicellulose are carbohydrates that can be broken down into fermentable sugars. The cellulosic and hemicellulosic portions of plant biomass are processed separately because they have different structures and sugar content. Cellulose consists of long chains of glucose molecules (simple 6-carbon sugars) arranged into a solid, three-dimensional, crystalline structure. Hemicellulose is a branched polymer composed primarily of xylose molecules (simple 5-carbon sugars) and some other sugars. Lignin, a rigid aromatic polymer, is not a

carbohydrate and cannot be converted into ethanol.

Efficiently separating and breaking down the different polymers in cellulosic biomass is an important challenge that is not an issue for corn ethanol production. One multistep process for converting cellulosic biomass to ethanol is outlined below. See [Applying Genomics for New Energy Resources: From Biomass to Cellulosic Ethanol](#) for an illustrated description of key steps in the conversion process.

1. **Mechanical Preprocessing.** Dirt and debris are removed from incoming biomass (e.g., bales of corn stover, wheat straw, or grasses), which is shredded into small particles.
2. **Pretreatment.** Heat, pressure, or acid treatments are applied to release cellulose, hemicellulose, and lignin and to make cellulose more accessible to enzymatic breakdown (hydrolysis). Hemicellulose is hydrolyzed into a soluble mix of 5- and 6-carbon sugars. A small portion of cellulose may be converted to glucose. If acid treatments are used, toxic by-products are neutralized by the addition of lime. Since cellulose biomass can come from many different sources (e.g., grasses, wheat straw, corn stover, paper products, hardwood, softwood), a single pretreatment process suitable for all forms of biomass does not exist.
3. **Solid-Liquid Separation.** The liquefied syrup of hemicellulose sugars is separated from the solid fibers containing crystalline cellulose and lignin.
4. **Fermentation of Hemicellulosic Sugars.** Through a series of biochemical reactions, bacteria convert xylose and other hemicellulose sugars to ethanol.
5. **Enzyme Production.** Some of the biomass solids are used to produce cellulase enzymes that break down crystalline cellulose. The enzymes are harvested from cultured microbes. Purchasing enzymes from a commercial supplier would eliminate this step.
6. **Cellulose Hydrolysis.** The fiber residues containing cellulose and lignin are transferred to a fermentation tank where cellulase enzymes are applied. A cocktail of different cellulases work together to attack crystalline cellulose, pull cellulose chains away from the crystal, and ultimately break each cellulose chain into individual glucose molecules.
7. **Fermentation of Cellulosic Sugars (Glucose).** Yeast or other microorganisms consume glucose and generate ethanol and carbon dioxide as products of the glucose fermentation pathway.
8. **Distillation.** Dilute ethanol broth produced during the fermentation of hemicellulosic and cellulosic sugars is distilled to remove water and concentrate the ethanol. Solid residues containing lignin and microbial cells can be burned to produce heat or used to generate electricity consumed by the ethanol-production process. Alternately, the solids could be converted to coproducts (e.g., animal feed, nutrients for crops).
9. **Dehydration.** The last remaining water is removed from the distilled ethanol.

## What are key biological barriers to cellulosic ethanol

## **production?**

Compared to cornstarch ethanol production, several factors make cellulosic ethanol production more costly and less efficient. One important barrier is lower sugar yields due to the heterogeneous and recalcitrant nature of cellulosic biomass. More effort is needed to pretreat and solubilize hemicellulose and cellulose because they are locked into a rigid cell-wall structure with lignin. Harsher thermochemical pretreatments generate chemical by-products that inhibit enzyme hydrolysis and decrease the productivity of fermentative microbes. The crystallinity of cellulose also makes it more difficult for aqueous solutions of enzymes to convert cellulose to glucose.

Another barrier is the mix of sugars generated from hemicellulose hydrolysis. Microorganisms that can ferment both 5- and 6-carbon sugars exist, but they have lower production rates and exhibit less tolerance for the end-product ethanol. Broth produced from a mix of 5- and 6-carbon sugars is about 6% ethanol instead of 10 to 14% ethanol produced from cornstarch glucose fermentation.

Overcoming these and other barriers will require a more complete understanding of several biological factors that impact the conversion process:

- Understanding what aspects of plant cell-wall structure and composition make some plant materials easier to break down than others.
- Investigating regulatory mechanisms that control cell-wall synthesis so that new bioenergy crops optimized for efficient biomass breakdown can be developed. For example, minimizing lignin content would improve enzyme access to cellulose during the hydrolysis step, thus increasing sugar yields.
- Surveying natural microbial communities to discover and analyze a more diverse range of enzymes that can break down cellulose, hemicellulose, and lignin. Perhaps novel enzymes capable of breaking down lignin and hemicellulose could be used to reduce the severity and improve the effectiveness of pretreatment.
- Creating new enzyme mixtures and analyzing their collective activities to determine the best combinations needed for rapid and complete breakdown of different components of biomass.
- Identifying the many genes that determine the most-desirable traits for fermentative microbes and understanding how these genes are regulated. Some of these traits include tolerance of higher ethanol concentrations, improved uptake and conversion of all sugars generated from biomass hydrolysis, elimination of unnecessary metabolic pathways, and achieving optimal fermentation productivity at higher temperatures to prevent contamination. Identifying these genes and understanding how they are controlled will be critical to developing the ideal fermentative microbe that possesses all these traits.
- Integrating all hydrolysis and fermentation steps into a single microbe or stable mixed culture to streamline the entire process and reduce costs.

## **How can Genomics:GTL improve production of cellulosic ethanol and other biofuels?**

Genomics:GTL (GTL) will provide systems-level biological investigations needed to rapidly develop new crops designed for bioenergy applications and to determine genetic makeup and functional capabilities of such microbial communities involved in biomass decomposition and sugar fermentation. Some advanced systems biology capabilities that GTL can provide include:

- Using advanced sequencing capabilities at DOE's Joint Genome Institute to sequence and analyze the genomes of crop plants, fermentative microbes, and microbial communities involved in biomass decomposition and soil productivity.
- High-throughput analysis of genes and proteins expressed by plants and microbes used to produce cellulosic ethanol and characterization of the conditions and regulatory systems that control expression.
- Comprehensive analysis of metabolites in plants and microbes to model cellular metabolism and define metabolic pathways relevant to biomass breakdown or ethanol fermentation.
- State-of-the-art imaging technologies covering a wide range of spatial scales to track enzymes in cells and elucidate molecular structure of plant cell walls.
- Advanced computational tools that will integrate large quantities of diverse biological data and develop predictive computer-based models of plant and microbial systems.

## Related Links

### Overview of U.S. Ethanol Industry

- [Annual Industry Outlook](#). Renewable Fuels Association

### Ethanol Production from Corn

- [How Ethanol Is Made](#). Renewable Fuels Association
- [How Is Ethanol Made?](#) American Coalition for Ethanol

### Ethanol Production from Cellulosic Biomass

- [ABC's of Biofuels](#). U.S. DOE Office of Energy Efficiency and Renewable Energy Biomass Program
- [Cellulose Ethanol Process Overview](#). Iogen Corporation

### Reports Promoting Increased Ethanol Production

- [Ending the Energy Stalemate: A Bipartisan Strategy to Meet America's Energy Challenges](#). National Commission on Energy Policy
- [Ethanol From Biomass: America's 21st Century Transportation Fuel Recommendations \(PDF\)](#). Governors' Ethanol Coalition
- [Growing Energy: How Biofuels Can Help End America's Oil Dependence](#).

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